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(71) Applicant (for all designated States except US): **ZYVEX CORPORATION** [US/US]; 1321 N. Plano Road, Richardson, TX 75081 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CHEN, Jian** [CN/US]; 411 Buckingham, #434, Richardson, TX 75081 (US). **RAJAGOPAL, Ramasubramaniam** [IN/US]; 2600 East Renner Road, #163, Richardson, TX 75082 (US).

(74) Agents: **MCCOMBS, David L.** et al.; Haynes and Boone, LLP, Suite 3100, 901 Main Street, Dallas, TX 75202 (US).

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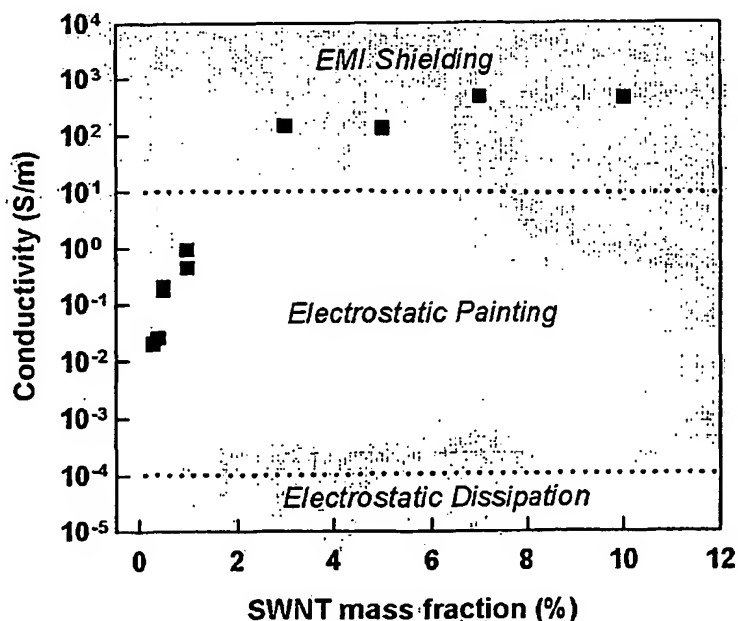
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[Continued on next page]

(54) Title: **NANOCOMPOSITES AND METHODS THERETO**



(57) Abstract: Electrical, thermal and mechanical applications are provided for nanocomposite materials having low percolation thresholds for electrical conductivity, low percolation thresholds for thermal conductivity, or improved mechanical properties.

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NANOCOMPOSITES AND METHODS THERE TO

Field of the Invention

[0001] The present patent application relates generally to the technical field of nanomaterial-based nanocomposites and their applications.

Background of the Invention

[0002] A carbon nanotube can be visualized as a sheet of hexagonal graph paper rolled up into a seamless tube and joined. Each line on the graph paper represents a carbon-carbon bond, and each intersection point represents a carbon atom.

[0003] In general, carbon nanotubes are elongated tubular bodies which are typically only a few atoms in circumference. The carbon nanotubes are hollow and have a linear fullerene structure. The length of the carbon nanotubes potentially may be millions of times greater than their molecular-sized diameter. Both single-walled carbon nanotubes (SWNTs), as well as multi-walled carbon nanotubes (MWNTs) have been recognized.

[0004] Carbon nanotubes (also referred to as "CNTs") are currently being proposed for a number of applications since they possess a very desirable and unique combination of physical properties relating to, for example, strength and weight. Carbon nanotubes have also demonstrated electrical conductivity (Yakobson, B.I., *et al.*, *American Scientist*, 85, (1997), 324-337; and Dresselhaus, M.S., *et al.*, *Science of Fullerenes and Carbon Nanotubes*, (1996), San Diego, Academic Press, 902-905). For example, carbon nanotubes conduct heat and electricity better than copper or gold and have 100 times the tensile strength of steel, with only a sixth of the weight of steel. Carbon nanotubes may be produced having extraordinary small size. For example, carbon nanotubes are being produced that are approximately the size of a DNA double helix (or approximately 1/50,000th the width of a human hair).

[0005] Considering the excellent properties of carbon nanotubes, they are well suited for a variety of uses, such as building computer circuits, reinforcing composite materials, and even to delivering medicine. In addition, carbon nanotubes may be useful in microelectronic device applications, which often demand high thermal conductivity, small dimensions, and lightweight. One application of carbon nanotubes that has been recognized from their use in flat-panel displays uses electron field-emission technology (since carbon nanotubes can be good conductors and electron emitters). Further applications that have been recognized include electromagnetic shielding, for cellular phones and laptop computers, radar absorption for stealth aircraft, nano-electronics (including memories in new generations of computers), and use as high-strength, lightweight, multifunctional composites.

[0006] However, attempts to use carbon nanotubes in composite materials have produced results that are far less than what is possible because of poor dispersion of nanotubes and agglomeration of the nanotubes in the host material. Pristine SWNTs are generally insoluble in common solvents and polymers, and difficult to chemically functionalize without altering the nanotube's desirable intrinsic properties.

Techniques, such as physical mixing, that have been successful with larger scale additives to polymers, such as glass fibers, carbon fibers, metal particles, etc. have failed to achieve good dispersion of CNTs. Two common approaches have been used previously to disperse the SWNTs in a host polymer:

1) Dispersing the SWNTs in a polymer solution by lengthy sonication (up to 48 h, M. J. Biercuk, *et al.*, *Appl. Phys. Lett.* 80, 2767 (2002)), and

2) In situ polymerization in the presence of SWNTs.

[0007] Lengthy sonication of approach 1), however, can damage or cut the SWNTs, which is undesirable for many applications. The efficiency of approach 2), is determined by the degree of dispersion of the nanotubes in solution which is very poor and is highly dependent on the specific polymer. For example, it works better for polyimide (Park, C. *et al.*, *Chem. Phys. Lett.*, 364, 303(2002)) than polystyrene (Barraza, H.J. *et al.*, *Nano Ltrs.*, 2, 797 (2002)).

[0008] Although CNTs have exceptional physical properties, incorporating them into other materials has been inhibited by the surface chemistry of carbon. Problems such as phase separation, aggregation, poor dispersion within a matrix, and poor adhesion to the host must be overcome.

[0009] A process of noncovalent functionalization and solubilization of carbon nanotubes is described by Chen, J. *et al.* (*J. Am. Chem. Soc.*, 124, 9034 (2002)) which process results in excellent nanotube dispersion. SWNTs were solubilized in chloroform with poly(phenyleneethynylene)s (PPE) along with vigorous shaking and/or short bath-sonication as described by Chen *et al.* (*ibid*) and in U.S. patent application US 2004/0034177 published February 19, 2004, having USSN 10/255,122, filed September 24, 2002, and U.S. patent application USSN 10/318,730 filed December 13, 2002. Composites of such functionalized and solubilized carbon nanotubes with the host polymers polycarbonate or polystyrene were fabricated and certain mechanical properties of such composites were reported in U.S. patent application US 2004/0034177 published February 19, 2004, USSN 10/255,122, filed September 24, 2002, and in U.S. patent application USSN 10/318,730 filed December 13, 2002.

[0010] The present inventors have addressed the problem of nanocomposites having nonuniform dispersion of nanomaterials in host polymer matrices that cause undesirable consequences to the composite material such as loss of strength, particle generation, increased viscosity, loss of processability, or other material degradation, and provide herein nanocomposites having improved properties.

Summary of the Invention

[0011] The present invention provides nanocomposites of functionalized, solubilized nanomaterials and host matrices where the nanocomposites provide increased electrical conductivity with lower electrical percolation thresholds, increased thermal conductivity with lower thermal percolation thresholds, or an improved mechanical property as compared to those of nanocomposites comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial. The low percolation thresholds demonstrate that a high dispersion of the nanomaterials in host matrices is achieved. Further, since a small amount of functionalized solubilized nanomaterial is needed to achieve increased conductivity or

improved properties of a host matrix, the host matrix's other desired physical properties and processability are not compromised.

[0012] A nanocomposite comprising a host matrix comprising polymer matrix or nonpolymer matrix and functionalized, solubilized nanomaterial dispersed within the host matrix is an embodiment of the invention. The nanocomposite has an electrical conductivity percolation threshold or a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial. The host matrix may be an organic polymer matrix, an inorganic polymer matrix, or a nonpolymer matrix, as described *infra*, or a combination thereof.

[0013] A further embodiment of the invention is the above-cited nanocomposite wherein the functionalized, solubilized nanomaterial of the nanocomposite is a first filler and the nanocomposite further comprises a second filler to form a complex nanocomposite. In this embodiment, the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and the second filler is other than a functionalized, solubilized nanomaterial.

[0014] A nanocomposite comprising a host matrix of polymer matrix or nonpolymer matrix, wherein the polymer matrix is other than polystyrene and polycarbonate, and functionalized, solubilized nanomaterial dispersed within the host matrix is a further embodiment of the invention. The nanocomposite has a mechanical property that is enhanced as compared to that of a nanocomposite comprising the host matrix and the nanomaterial other than the functionalized, solubilized nanomaterial. The nanocomposite may further comprise a second host polymer matrix wherein the functionalized, solubilized nanomaterial is dispersed within the first and second host polymer matrices. Further, where the functionalized, solubilized nanomaterial of the nanocomposite is a first filler, the nanocomposite may further comprise a second filler to form a complex nanocomposite wherein the second filler is other than a functionalized, solubilized nanomaterial.

[0015] A further nanocomposite of the present invention comprises a polystyrene, and a functionalized, solubilized nanomaterial dispersed within the polystyrene. Such a nanocomposite has a mechanical property that is enhanced as compared to that of a nanocomposite comprising the host matrix and the nanomaterial other than the functionalized, solubilized nanomaterial. The nanocomposite may further comprise a second host polymer matrix, wherein the functionalized, solubilized nanomaterial is dispersed within the first and second host polymer matrices.

[0016] In one embodiment, a nanocomposite comprises a host matrix comprising a first polymer matrix and a second polymer matrix and functionalized, solubilized nanomaterial dispersed within the host matrix wherein the first polymer matrix is polycarbonate.

[0017] A method of increasing electrical or thermal conductivity of a host matrix comprising a polymer matrix or a nonpolymer matrix comprises dispersing functionalized, solubilized nanomaterial within host matrix material to form a nanocomposite. In this embodiment, the nanocomposite has an electrical conductivity percolation threshold or a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized,

solubilized nanomaterial. The host matrix material may be the host matrix or a monomer of a host polymer matrix and, in such an embodiment, the method further comprises the step of polymerizing the host polymer matrix material in the presence of the functionalized, solubilized nanomaterial. In a further embodiment, the host matrix is a first host polymer matrix and the method further comprises dispersing a second host polymer matrix material with functionalized, solubilized nanomaterial and with first host polymer matrix material to form a nanocomposite comprising a first host polymer matrix and a second host polymer matrix. In one embodiment, functionalized, solubilized nanomaterial is a first filler, and the dispersing further comprises dispersing a second filler within host matrix material to form a complex nanocomposite, wherein the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and wherein the second filler is other than a functionalized, solubilized nanomaterial.

[0018] A method of improving a mechanical property of a host matrix comprising a polymer matrix or a nonpolymer matrix, wherein the host matrix is other than polystyrene or polycarbonate is an aspect of the present invention. The method comprises dispersing functionalized, solubilized nanomaterial within host matrix material to form a nanocomposite wherein the nanocomposite has an improved mechanical property compared to that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial. The host matrix material may be the host matrix or comprise a monomer of the host matrix and the method then further comprises the step of polymerizing the host matrix material in the presence of the functionalized, solubilized nanomaterial. The method may further comprise dispersing a second host polymer matrix material with functionalized, solubilized nanomaterial and with first host polymer matrix material to form a nanocomposite comprising a first host polymer matrix and a second host polymer matrix. Further, when the functionalized, solubilized nanomaterial is a first filler, the dispersing may further comprise dispersing a second filler within host matrix material to form a complex nanocomposite wherein the second filler is other than a functionalized, solubilized nanomaterial.

[0019] A method of improving a mechanical property of a polystyrene comprises dispersing functionalized, solubilized nanomaterial within styrene polymeric material to form a nanocomposite wherein the nanocomposite has an improved mechanical property compared to that of a nanocomposite comprising the polystyrene and nanomaterial other than the functionalized, solubilized nanomaterial. A second host matrix or a second filler may be added to produce further embodiments for improving a mechanical property of a polystyrene.

[0020] A method of improving a mechanical property of a host matrix comprising a first polymer matrix and a second polymer matrix wherein the first polymer matrix is polycarbonate is an aspect of the present invention. The method comprises dispersing functionalized, solubilized nanomaterial within host polymeric material to form a nanocomposite wherein the nanocomposite has an improved mechanical property compared to that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial. A second filler may be added to produce a complex nanocomposite.

[0021] An article of manufacture comprising a nanocomposite having an improved electrical, thermal, or mechanical property as described herein is a further embodiment of the invention. Further, a product produced by a method as described herein is an embodiment of the present invention.

Brief Description of the Drawings

[0022] For a more complete understanding of the present invention, reference is made to the following descriptions taken in conjunction with the accompanying drawings.

[0023] FIG. 1A is a scanning electron microscopy image showing the surface of PPE-SWNTs/polystyrene nanocomposite film prepared by an embodiment of the present invention using 5 wt% of SWNTs.

[0024] FIG. 1B is a scanning electron microscopy image showing the cross-section of PPE-SWNTs/polystyrene nanocomposite film prepared by an embodiment of the present invention using 5 wt% of SWNTs.

[0025] FIG. 2A shows room temperature electrical conductivity in siemens/meter (S/m) (also known as measured volume conductivity) of a PPE-SWNTs/polystyrene nanocomposite versus the SWNT weight loading for embodiments formed in accordance with the present invention. The dashed lines represent approximate conductivity lower bounds required for EMI shielding, electrostatic painting, and for electrostatic dissipation. At 0% mass fraction, the conductivity is about 10^{-14} S/m.

[0026] FIG. 2B shows room temperature conductivity of the PPE-SWNTs/polystyrene nanocomposite as a function of reduced mass fraction of SWNTs. The percolation threshold m_c is 0.045%.

[0027] FIG. 3A shows room temperature electrical conductivity of a PPE-SWNTs/polycarbonate nanocomposite versus SWNT weight loading prepared by an embodiment of the present invention. The dashed lines represent approximate conductivity lower bounds required for EMI shielding, electrostatic painting, and for electrostatic dissipation.

[0028] FIG. 3B shows room temperature conductivity of the PPE-SWNTs/polycarbonate nanocomposite as a function of reduced mass fraction of SWNTs. The percolation threshold m_c is 0.110%.

[0029] FIG. 4 shows a field-emission scanning electron microscopy image of a fracture surface at a broken end of a f-s-SWNTs polycarbonatenanocomposite film loaded at 1 wt% of SWNTs.

[0030] FIG. 5A and FIG. 5B show example heat transfer applications of a CNT-polymer composite in accordance with certain embodiments of the present invention. FIG. 5A shows an architecture typically used in laptop applications, and FIG. 5B shows an architecture typically used in desktop and server applications. The large arrow pointing upward indicates the primary heat transfer path in each architecture. See Example 2 for designation of components.

[0031] FIG. 6A shows tensile stress vs. tensile strain of pure polycarbonate film prepared by solution casting.

[0032] FIG. 6B shows tensile stress vs. tensile strain of f-s-SWNTs/polycarbonate film having 2 wt% SWNTs prepared by solution casting.

Description

[0033] Highly dispersed carbon nanotube/polymer nanocomposites were fabricated using functionalized, solubilized single-walled carbon nanotubes (f-s-SWNTs). Such nanocomposites have demonstrated, for example, electrical conductivity with very low percolation threshold (0.05-0.1 wt% of SWNT loading). A very low f-s-SWNT loading is needed to achieve conductivity levels required for various electrical applications without compromising the host polymer's other preferred physical properties and processability.

[0034] *Nanocomposite:* The term "nanocomposite," as used herein, means a noncovalently functionalized solubilized nanomaterial dispersed within a host matrix. The host matrix may be a host polymer matrix or a host nonpolymer matrix.

[0035] *Host polymer matrix:* The term "host polymer matrix," as used herein, means a polymer matrix within which the nanomaterial is dispersed. A host polymer matrix may be an organic polymer matrix or an inorganic polymer matrix, or a combination thereof.

[0036] Examples of a host polymer matrix include a nylon, polyethylene, epoxy resin, polyisoprene, sbs rubber, polydicyclopentadiene, polytetrafluoroethylene, poly(phenylene sulfide), poly(phenylene oxide), silicone, polyketone, aramid, cellulose, polyimide, rayon, poly(methyl methacrylate), poly(vinylidene chloride), poly(vinylidene fluoride), carbon fiber, polyurethane, polycarbonate, polyisobutylene, polychloroprene, polybutadiene, polypropylene, poly(vinyl chloride), poly(ether sulfone), poly(vinyl acetate), polystyrene, polyester, polyvinylpyrrolidone, polycyanoacrylate, polyacrylonitrile, polyamide, poly(aryleneethynylene), poly(phenyleneethynylene), polythiophene, thermoplastic, thermoplastic polyester resin (such as polyethylene terephthalate), thermoset resin (e.g., thermosetting polyester resin or an epoxy resin), polyaniline, polypyrrole, or polyphenylene such as PARMAX®, for example, other conjugated polymers (e.g., conducting polymers), or a combination thereof.

[0037] Further examples of a host polymer matrix includes a thermoplastic, such as ethylene vinyl alcohol, a fluoroplastic such as polytetrafluoroethylene, fluoroethylene propylene, perfluoroalkoxyalkane, chlorotrifluoroethylene, ethylene chlorotrifluoroethylene, or ethylene tetrafluoroethylene, ionomer, polyacrylate, polybutadiene, polybutylene, polyethylene, polyethylenechlorinates, polymethylpentene, polypropylene, polystyrene, polyvinylchloride, polyvinylidene chloride, polyamide, polyamide-imide, polyaryletherketone, polycarbonate, polyketone, polyester, polyetheretherketone, polyetherimide, polyethersulfone, polyimide, polyphenylene oxide, polyphenylene sulfide, polyphthalamide, polysulfone, or polyurethane. In certain embodiments, the host polymer includes a thermoset, such as allyl resin, melamine formaldehyde, phenol-formaldehyde plastic, polyester, polyimide, epoxy, polyurethane, or a combination thereof.

[0038] Examples of inorganic host polymers include a silicone, polysilane, polycarbosilane, polygermane, polystannane, a polyphosphazene, or a combination thereof.

[0039] More than one host matrix may be present in a nanocomposite. By using more than one host matrix, mechanical, thermal, chemical, or electrical properties of a single host matrix nanocomposite are optimized by adding f-s-SWNTs to the matrix of the nanocomposite material. Example 4 *infra* provides

an example of such an embodiment where polycarbonate and epoxy are provided as host polymers in a nanocomposite material of the present invention. Addition of polycarbonate in addition to epoxy appears to reduce voids in a nanocomposite film as compared to a nanocomposite film with just epoxy as the host polymer. Such voids degrade the performance of nanocomposites.

[0040] In one embodiment, using two host polymers is designed for solvent cast epoxy nanocomposites where the f-s-SWNTs, the epoxy resin and hardener, and the polycarbonate are dissolved in solvents and the nanocomposite film is formed by solution casting or spin coating.

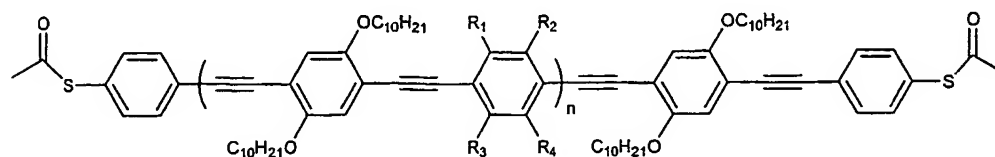
[0041] *Host nonpolymer matrix:* The term “host nonpolymer matrix,” as used herein, means a nonpolymer matrix within which the nanomaterial is dispersed. Examples of host nonpolymer matrices include a ceramic matrix (such as silicon carbide, boron carbide, or boron nitride), or a metal matrix (such as aluminum, titanium, iron, or copper), or a combination thereof. Functionalized solubilized SWNTs are mixed with, for example, polycarbosilane in organic solvents, and then the solvents are removed to form a solid (film, fiber, or powder). The resulting solid f-s-SWNTs/polycarbosilane nanocomposite is further converted to SWNTs/SiC nanocomposite by heating at 900-1600 °C either under vacuum or under inert atmosphere (such as Ar).

[0042] *Nanomaterial:* The term “nanomaterial,” as used herein, includes, but is not limited to, functionalized and solubilized multi-wall carbon or boron nitride nanotubes, single-wall carbon or boron nitride nanotubes, carbon or boron nitride nanoparticles, carbon or boron nitride nanofibers, carbon or boron nitride nanoropes, carbon or boron nitride nanoribbons, carbon or boron nitride nanofibrils, carbon or boron nitride nanoneedles, carbon or boron nitride nanosheets, carbon or boron nitride nanorods, carbon or boron nitride nanohorns, carbon or boron nitride nanocones, carbon or boron nitride nanoscrolls, graphite nanoplatelets, nanodots, other fullerene materials, or a combination thereof. The term “nanotubes” is used broadly herein and, unless otherwise qualified, is intended to encompass any type of nanomaterial. Generally, a “nanotube” is a tubular, strand-like structure that has a circumference on the atomic scale. For example, the diameter of single walled nanotubes typically ranges from approximately 0.4 nanometers (nm) to approximately 100 nm, and most typically have diameters ranging from approximately 0.7 nm to approximately 5 nm.

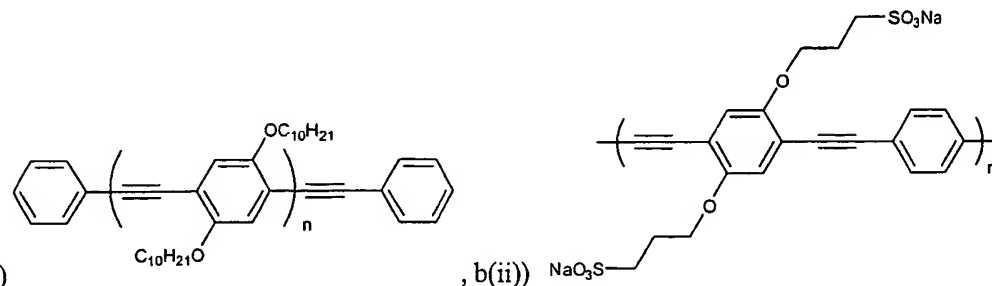
[0043] While the term “SWNTs,” as used herein, means single walled nanotubes, the term means that other nanomaterials as cited *supra* may be substituted unless otherwise stated herein.

[0044] *Functionalized, solubilized nanomaterial:* The term “functionalized, solubilized nanomaterial,” as used herein, means that the nanomaterial is solubilized by a nonwrapping, noncovalent functionalization with a rigid, conjugated polymer. Such functionalization and solubilization is exemplified by the process and compositions for carbon nanotubes of Chen, J. *et al.* (*J. Am. Chem. Soc.*, 124, 9034 (2002)) which process results in excellent nanotube dispersion and is described in U.S. patent application US 2004/0034177 published February 19, 2004, having USSN 10/255,122, filed September 24, 2002, and U.S. patent application USSN 10/318,730 filed December 13, 2002.

[0045] The term “rigid, conjugated polymer,” as used herein for functionalization and solubilization, contains a backbone portion for noncovalently bonding with a nanotube in a non-wrapping fashion. The backbone portion may comprise a group having the formula:

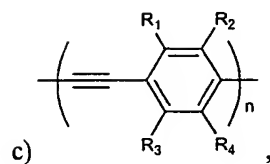


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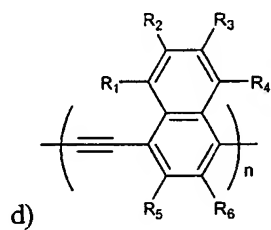


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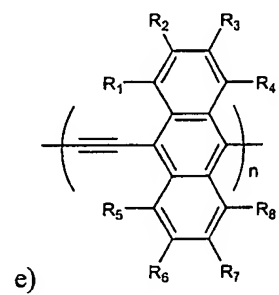
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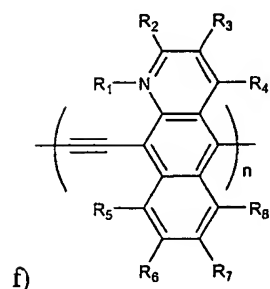
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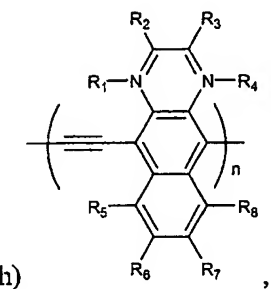
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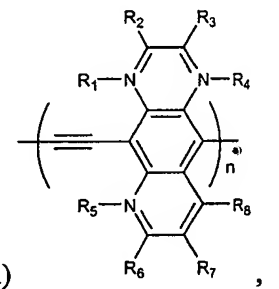
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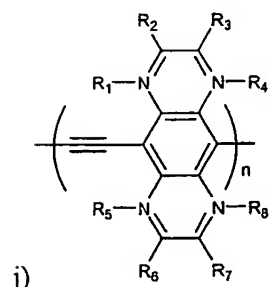
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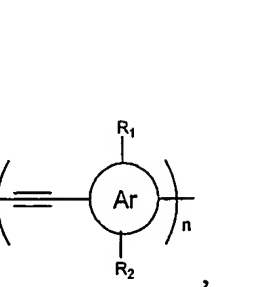
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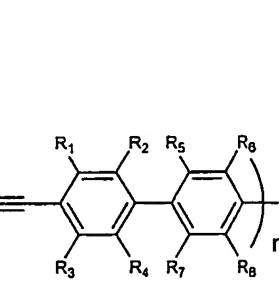
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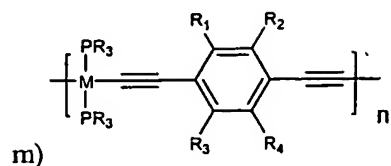
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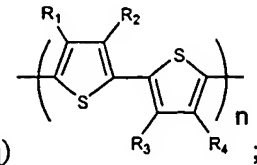
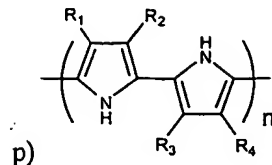
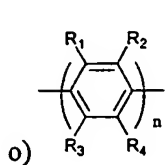
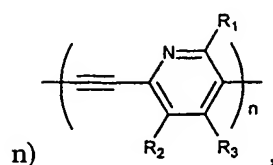
k)



l)



, wherein M is selected from the group consisting of Ni, Pd, and Pt,



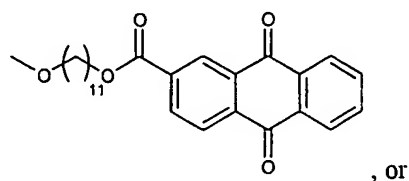
wherein each of R_1 - R_8 in the above-listed backbone portions a)-q) represents H, or F, or an R group bonded to the backbone via a carbon or an oxygen linkage as described *infra*.

[0046] For example, the backbone may comprise a poly(aryleneethynylene) of a *supra* wherein the R groups are as follows:

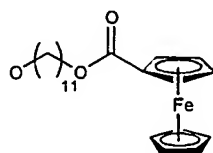
i) $R_1=R_4=H$ and $R_2=R_3=OC_{10}H_{21}$,

ii) $R_1=R_2=R_3=R_4=F$,

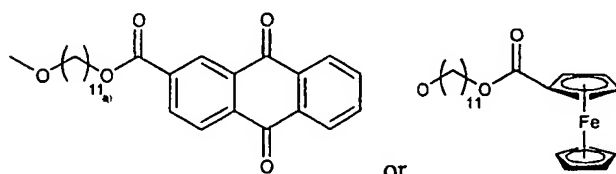
iii) $R_1=R_4=H$ and $R_2=R_3=$



iiii) $R_1=R_4=H$ and $R_2=R_3=$

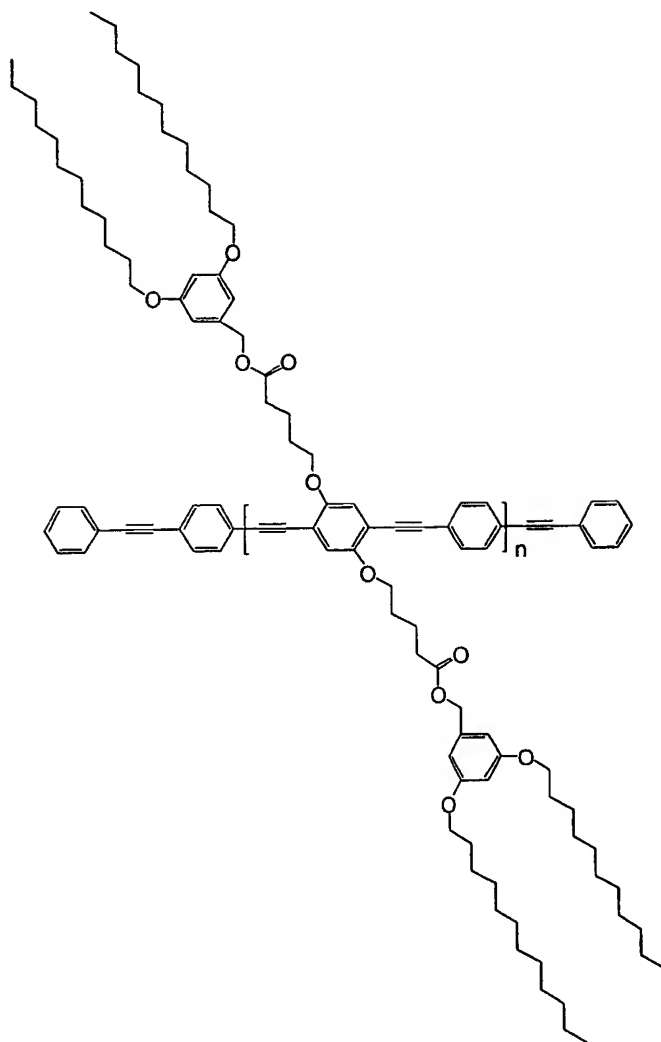


, or any combination thereof. That is, an R group may be

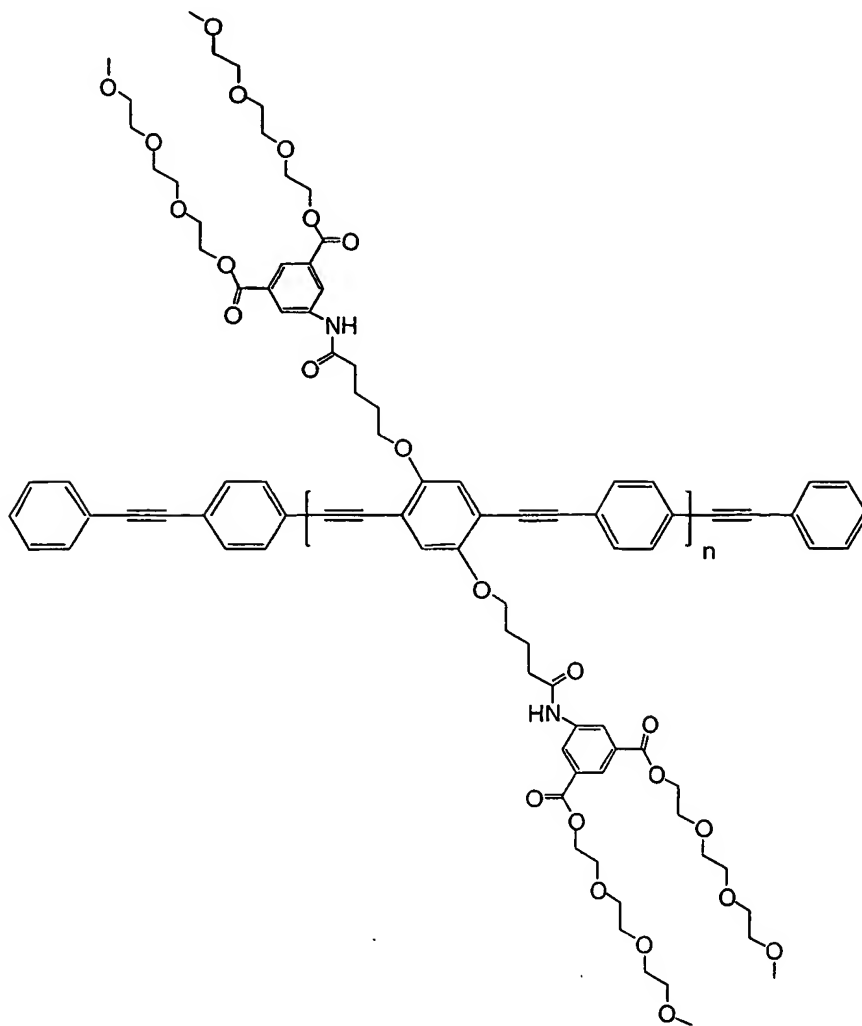


H, $OC_{10}H_{21}$, F,

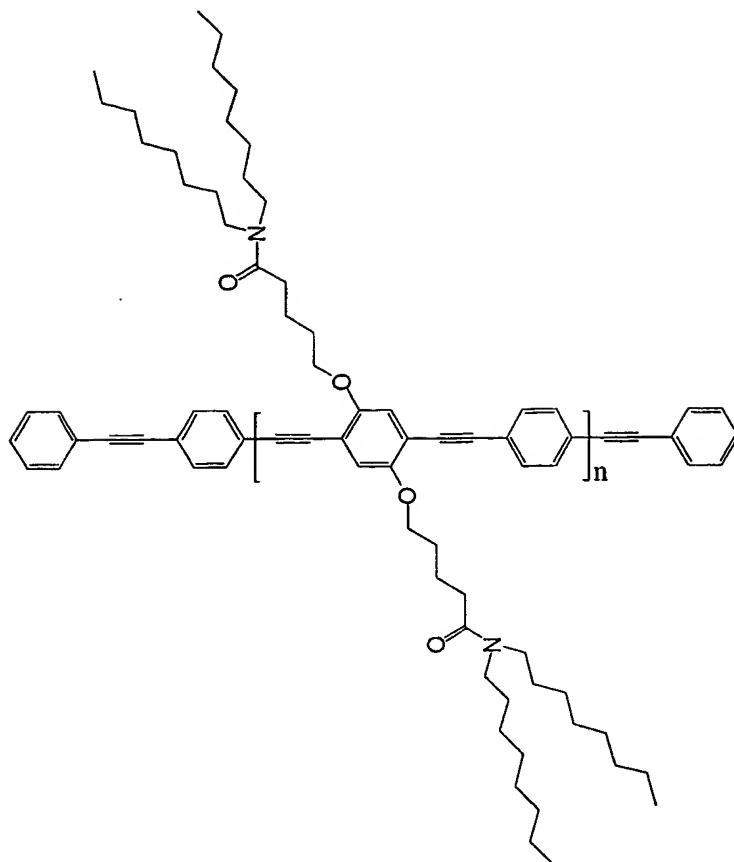
[0047] Further embodiments of a rigid, conjugated polymer include those having a backbone and R groups bonded to a backbone via an ether linkage as follows:



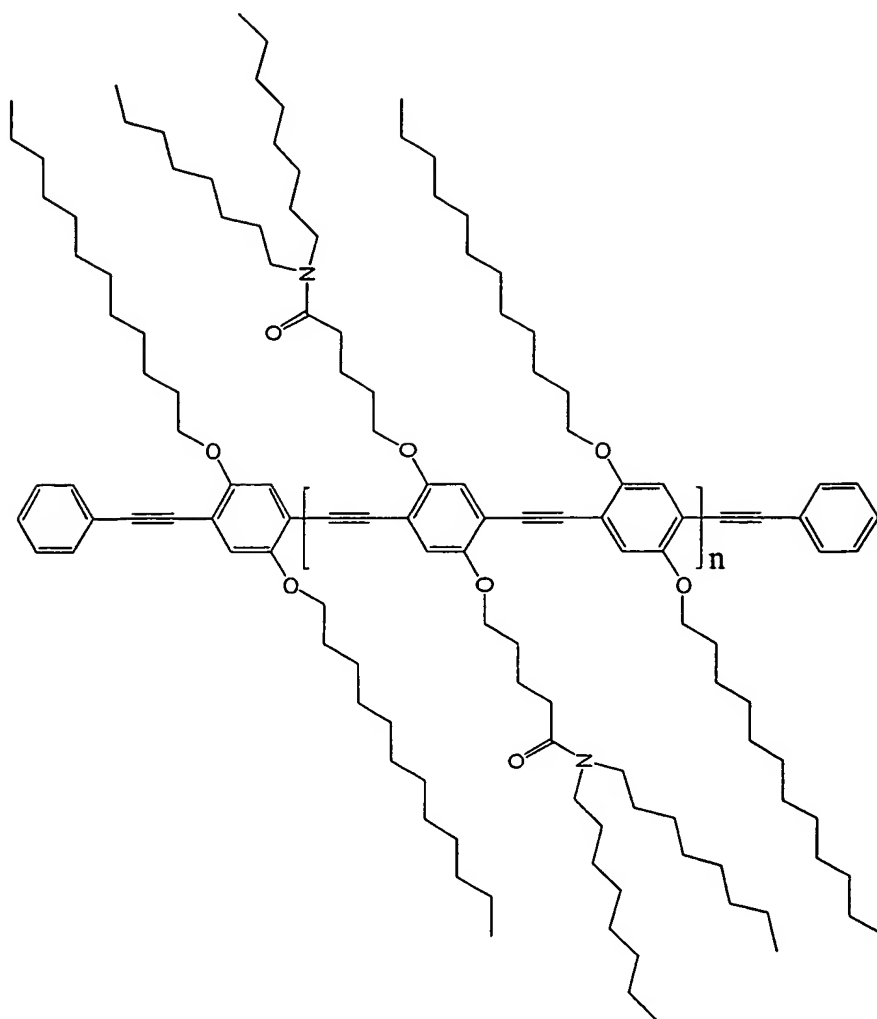
r),



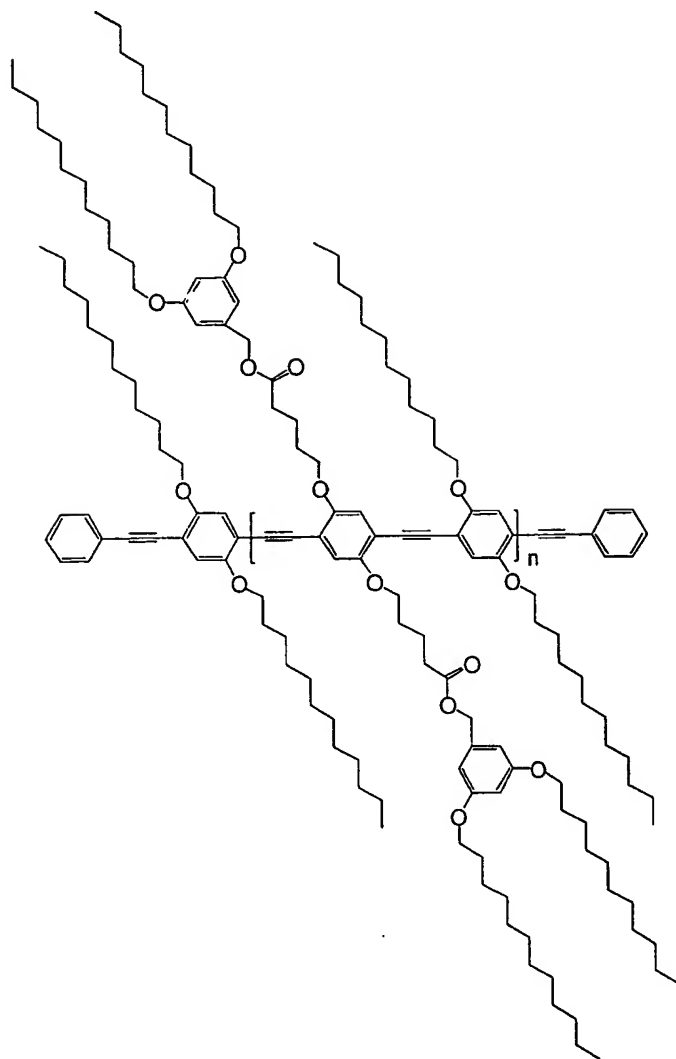
s),



t),

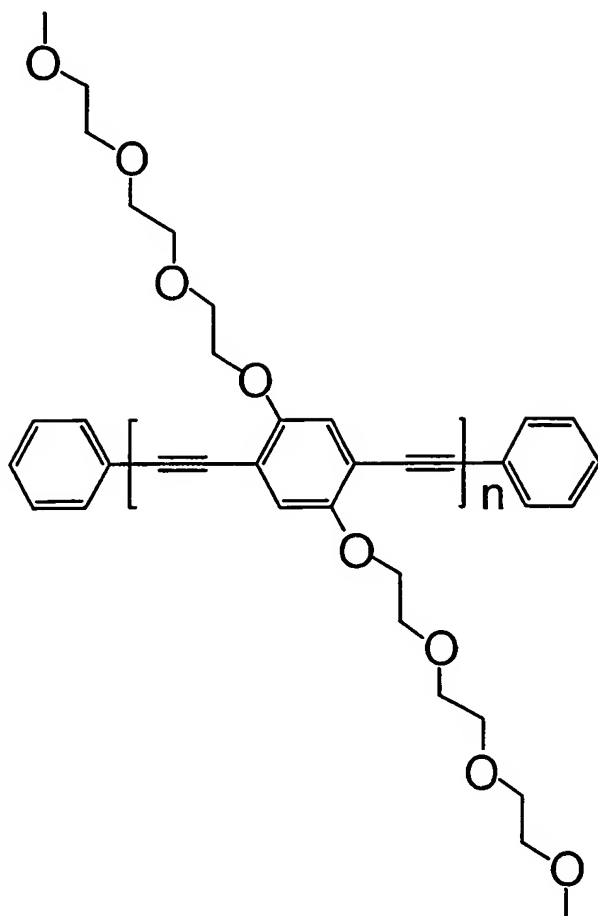


u),

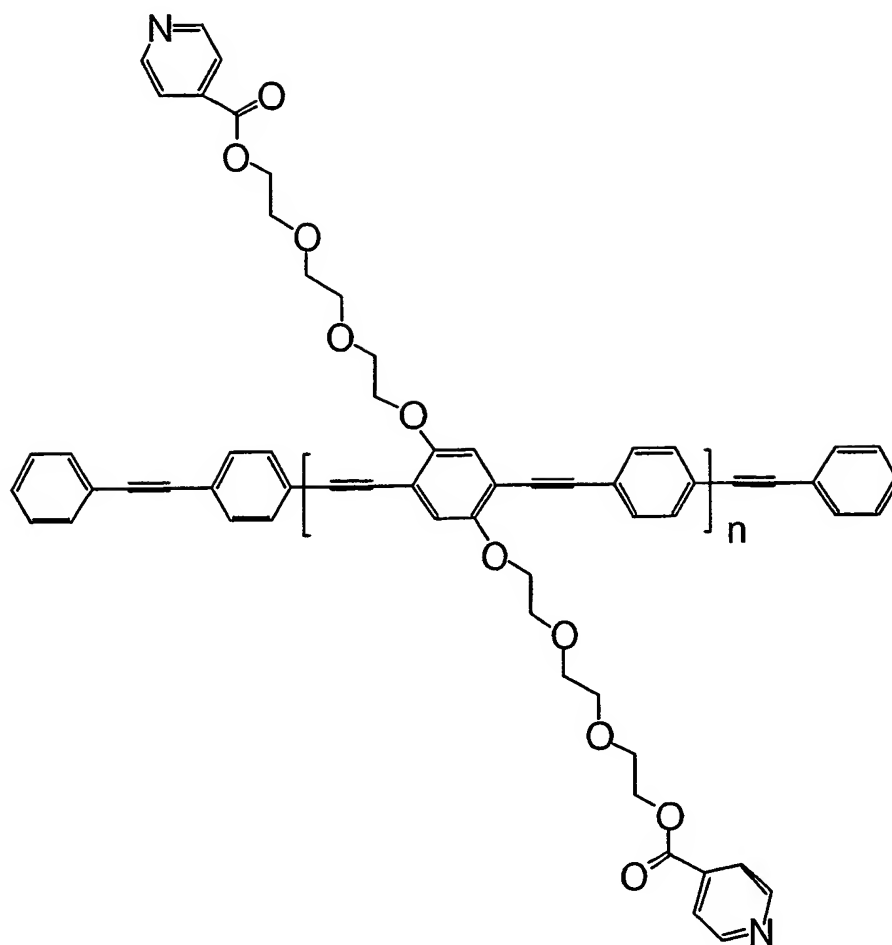


v),

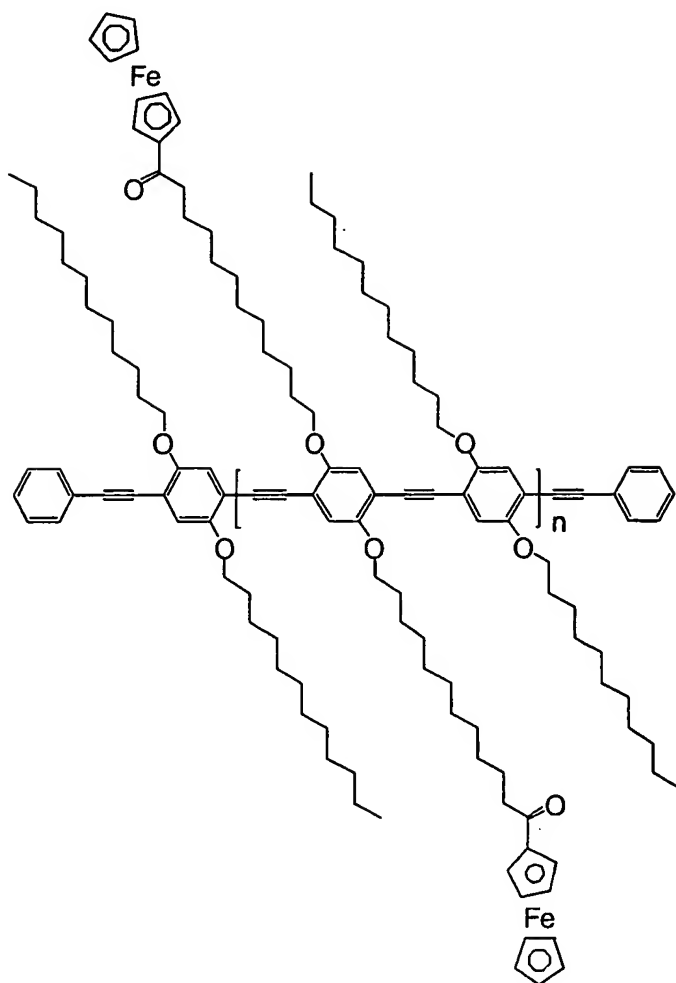
•



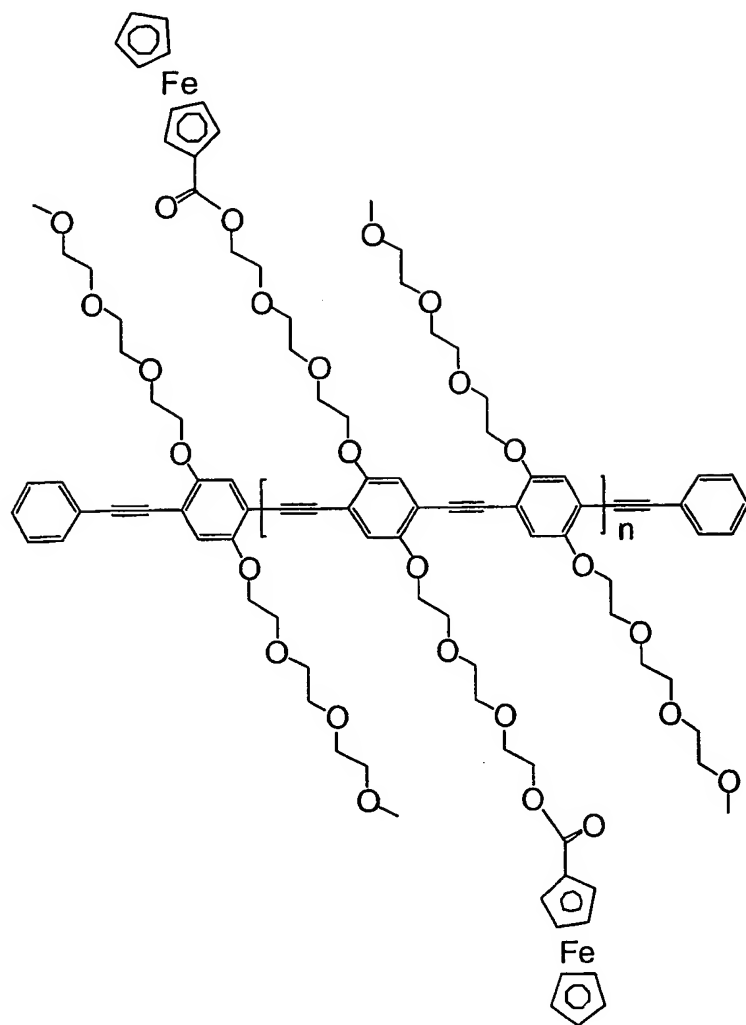
w),



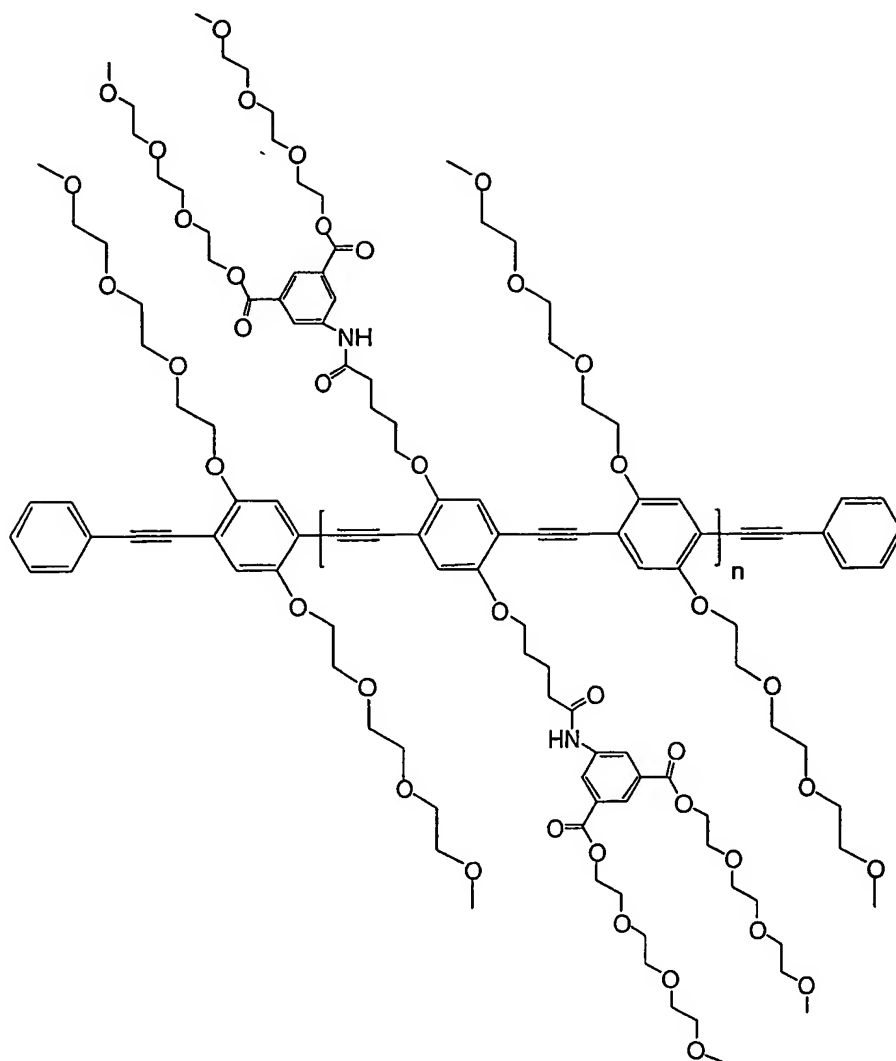
x),



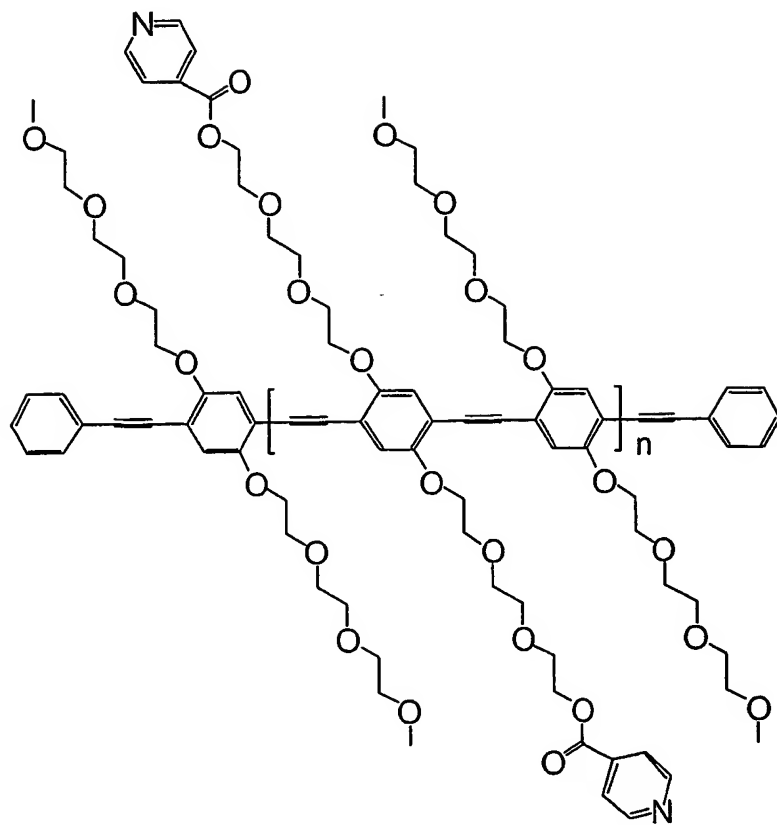
y),



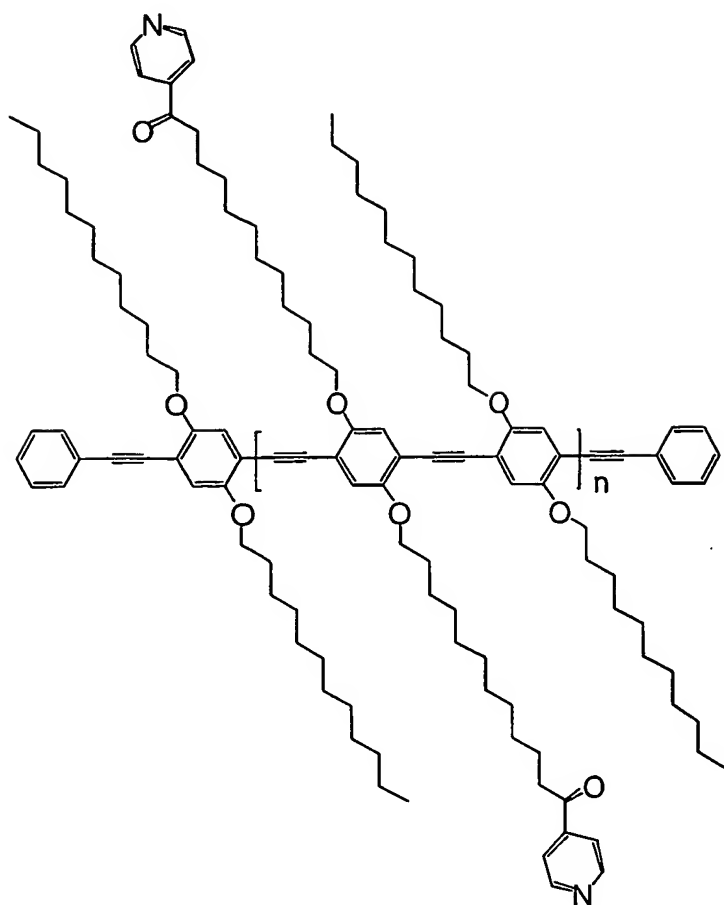
z),



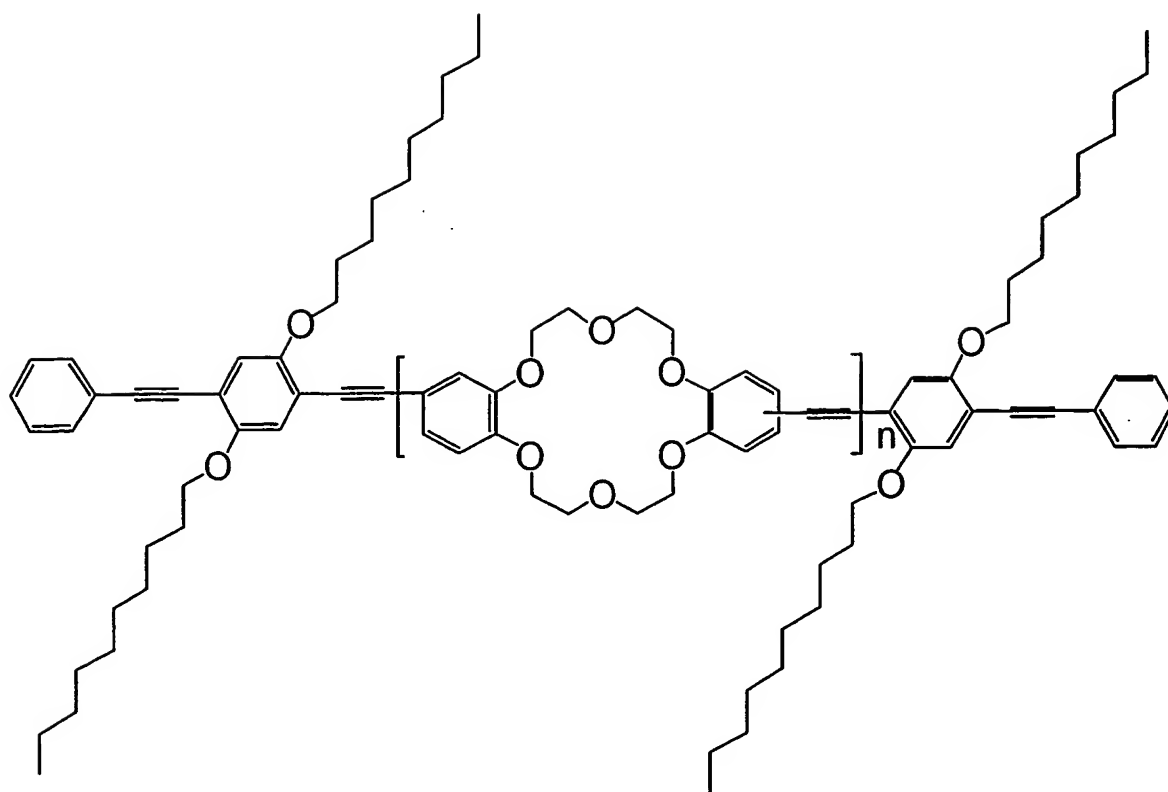
aa),



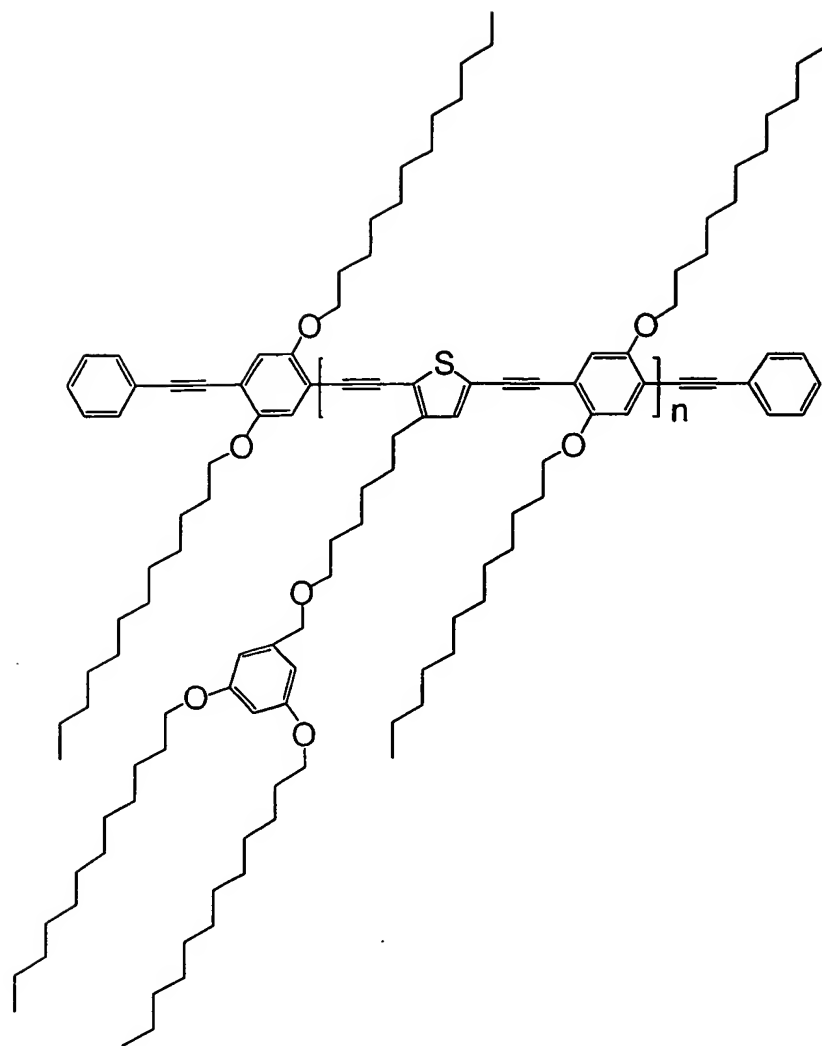
bb),



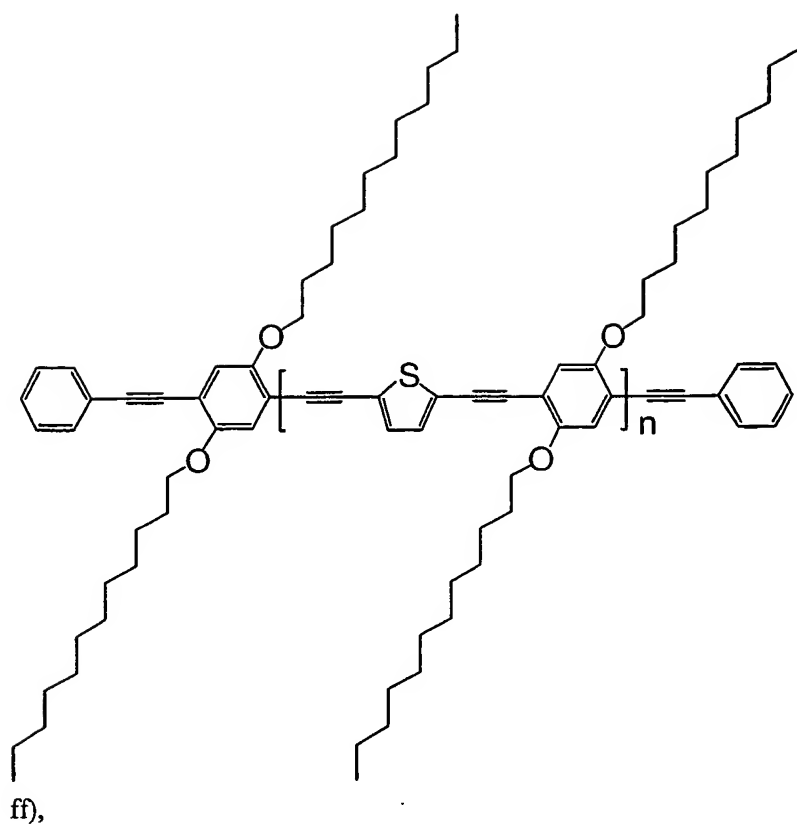
cc),

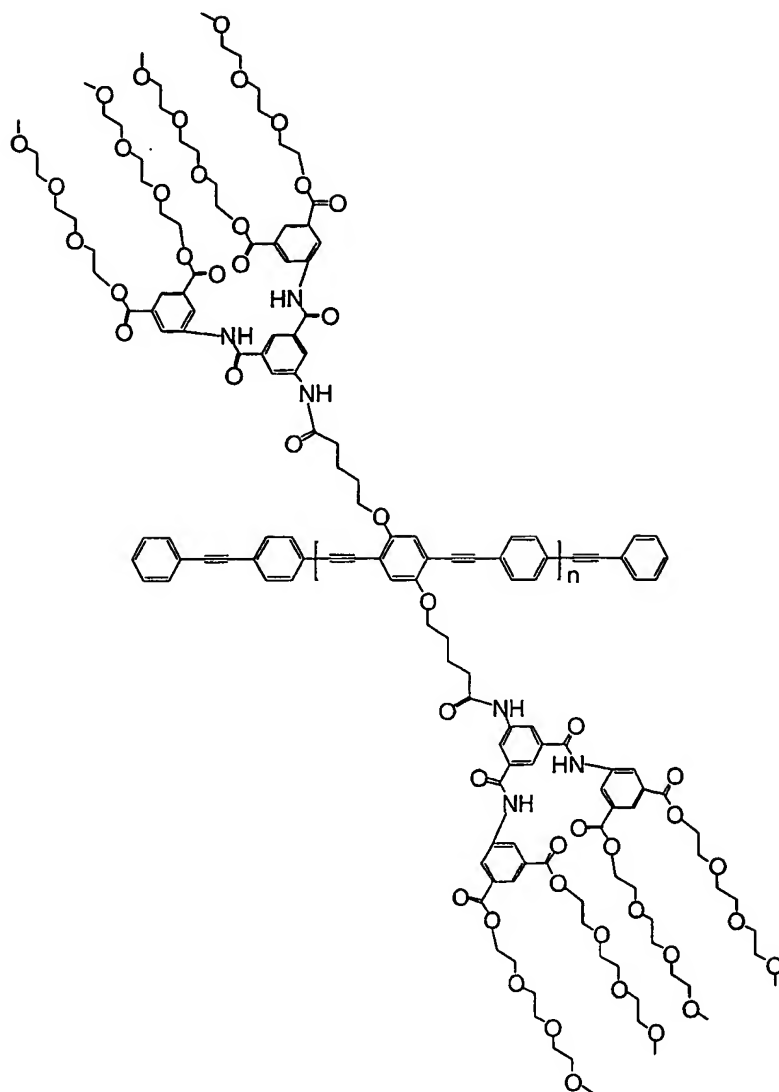


dd); or, in addition, a carbon linkage as shown in ee) or jj),

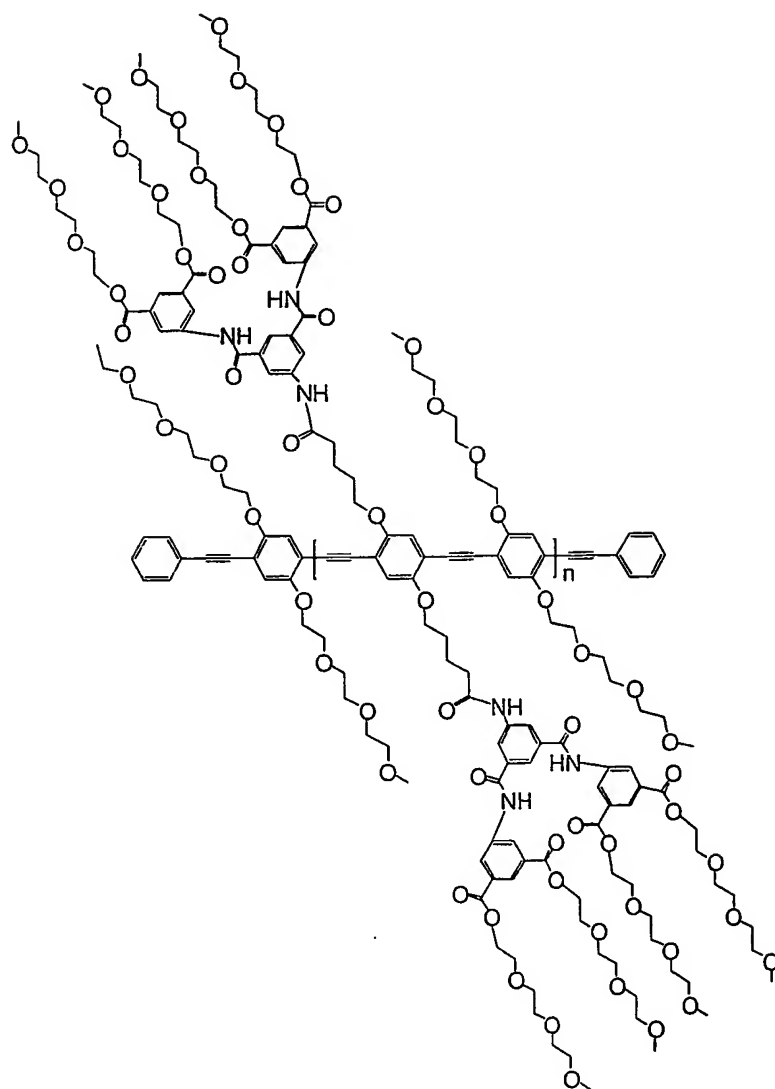


ee),

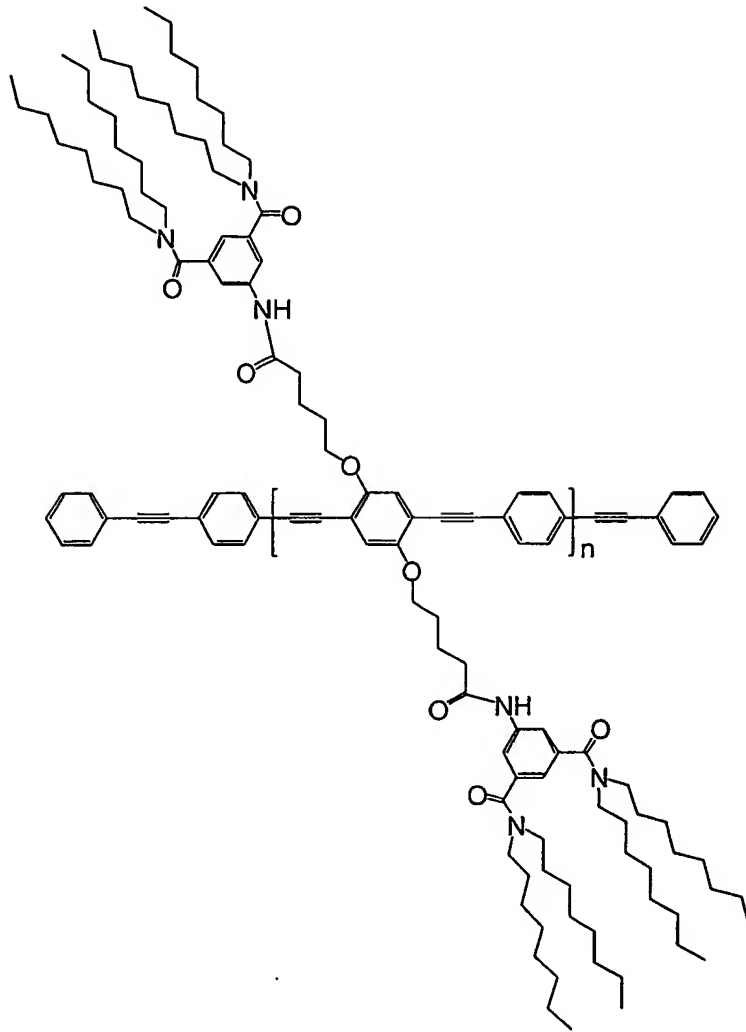




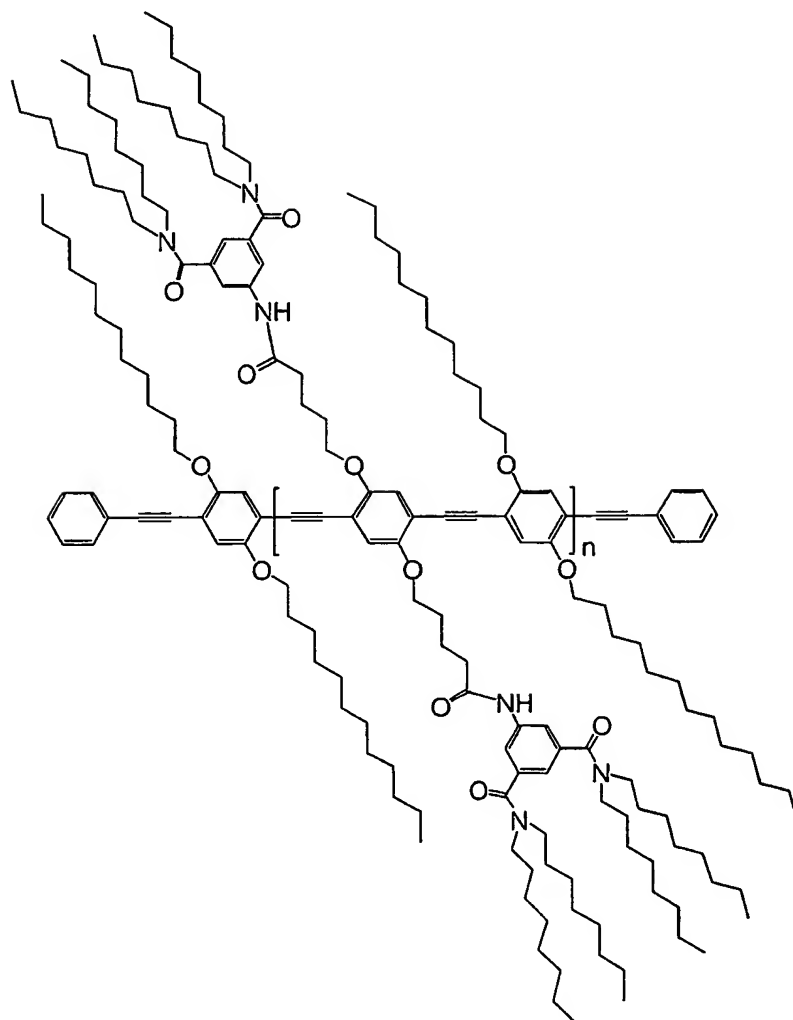
gg),



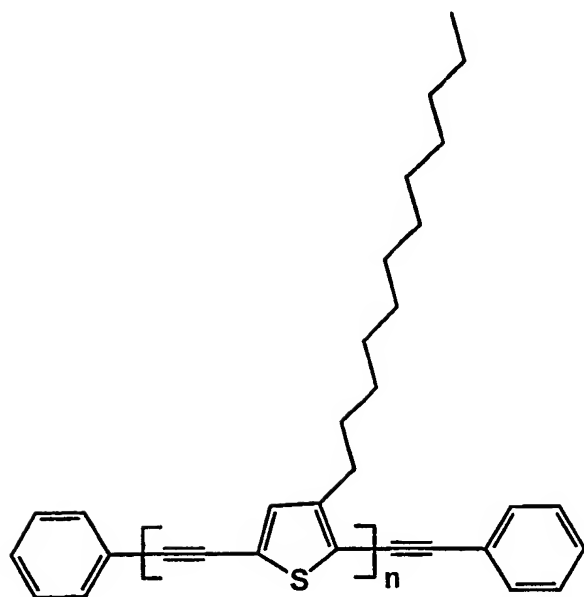
hh),



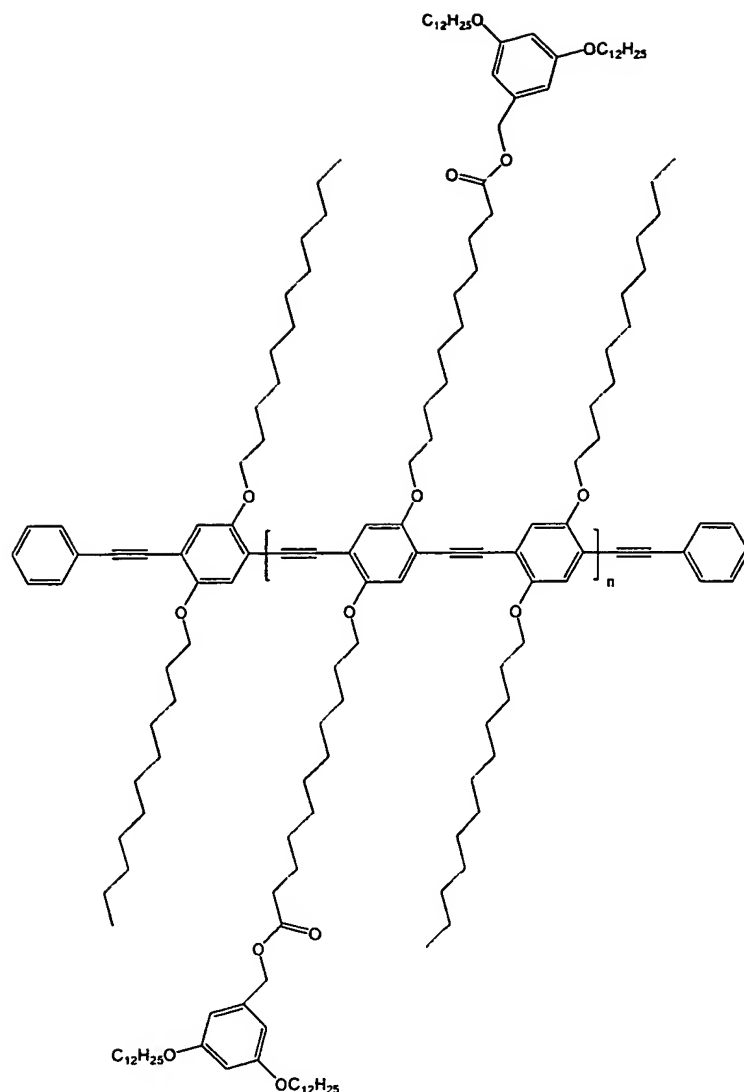
ii),



jj),



kk), or



11).

[0048] In an embodiment, the R group is designed to adjust the CNTs' solubility in various solvents, for example, using PPE polymers with linear or branched glycol side chains provides for high solubility of SWNTs in DMF or NMP, which further provides for uniform mixing of f-s-SWNTs with host polymers (for example, polyacrylonitrile) that are soluble in DMF or NMP, but not in halogenated solvents (such as chloroform). In further embodiments, the R groups bonded to the backbone via a carbon-carbon bond or an oxygen-carbon bond as described *supra* may have additional reactive species, i.e., functional groups, at the periphery of the R groups. The term "periphery," as used herein, means at the outer end of such R group side chains, away or distal from the backbone. Such functional groups include, for example, acetal, acid halide, acyl azide, aldehyde, alkane, anhydride, cyclic alkane, arene, alkene, alkyne, alkyl halide, aryl halide, amine, amide, amino acid, alcohol, azide, aziridine, azo compounds, calixarene, carbohydrate, carbonate, carboxylic acid, carboxylate, carbodiimide, cyclodextrin, crown ether, cryptand, diaminopyridine, diazonium compounds, ester, ether, epoxide, fullerene, glyoxal, imide, imine, imidoester, ketone, nitrile, isothiocyanate, isocyanate, isonitrile, lactone, maleimide, metallocene, NHS ester, nitroalkane, nitro compounds, nucleotide, oligosaccharide, oxirane, peptide, phenol,

phthalocyanine, porphyrin, phosphine, phosphonate, polyimine (2,2'-bipyridine, 1,10-phenanthroline, terpyridine, pyridazine, pyrimidine, purine, pyrazine, 1,8-naphthyridine, polyhedral oligomeric silsequioxane (POSS), pyrazolate, imidazolate, torand, hexapyridine, 4,4'-bipyrimidine, for example), pyridine, quaternary ammonium salt, quaternary phosphonium salt, quinone, Schiff base, selenide, sepulchrate, silane, sulfide, sulfone, sulfonyl chloride, sulfonic acid, sulfonic acid ester, sulfonium salt, sulfoxide, sulfur and selenium compounds, thiol, thioether, thiol acid, thio ester, thymine, or a combination thereof.

[0049] Peripheral functional groups at the ends of R groups distal to the backbone of the functionalized, solubilized nanotube enhance interaction between the functionalized, solubilized nanomaterial and the host matrix of composites of the present invention. Such peripheral functional groups are designed to improve the interfacial bonding between functionalized, solubilized CNTs and the host matrix. For example, using PPE polymers with reactive functional groups (such as epoxide, or amine, or pyridine) at the end of linear or branched side chains distal to the backbone provides for covalent bonding between f-s-SWNTs and an epoxy matrix, therefore increasing mechanical properties of an f-s-SWNTs/epoxy nanocomposite, for example. Further, using a PPE polymer with a thiol group at or near the end of a linear or branched side chain provides for enhanced interaction between f-s-SWNTs and gold or silver nanoparticles (host matrices), for example. A further example provides SWNTs functionalized with a PPE polymer having thymine at the end of a linear side chain. A fiber can then be assembled with SWNTs functionalized with such PPE polymers and with PPE polymers having diaminopyridine in the end of linear side chain by forming extensive parallel triple (three-point) hydrogen bonds.

[0050] While the term "f-s-SWNTs," as used herein, means functionalized, solubilized single walled nanotubes, the term means that other nanomaterials as cited *supra* may be substituted unless otherwise stated herein.

[0051] Rigid, conjugated polymers for functionalization include a poly(phenyleneethynylene) (PPE), poly(aryleneethynylene), or poly(3-decylthiophene), for example. Such functionalization provides for a solubility of carbon nanomaterial in solvents and lengthy sonication procedures are not needed. This non-wrapping functionalization is suitable for nanomaterial as described herein. Since the polymer is attached to the nanomaterial surface by noncovalent bonding instead of covalent bonding, the underlying electronic structure of the nanotubes and their key attributes are not affected.

[0052] *Complex nanocomposites:* Nanocomposites can themselves be used as a host matrix for a second filler to form a complex nanocomposites. Examples of a second filler include: continuous fibers (such as carbon fibers, carbon nanotube fibers, carbon nanotube nanocomposite fibers, KEVLAR® fibers, ZYLON® fibers, SPECTRA® fibers, nylon fibers, or a combination thereof, for example), discontinuous fibers (such as carbon fibers, carbon nanotube fibers, carbon nanotube nanocomposite fibers, KEVLAR® fibers, ZYLON® fibers, SPECTRA® fibers, nylon fibers, or a combination thereof, for example), nanoparticles (such as metallic particles, polymeric particles, ceramic particles, nanoclays, diamond particles, or a combination thereof, for example), and microparticles (such as metallic particles, polymeric particles, ceramic particles, clays, diamond particles, or a combination thereof, for example).

[0053] A number of existing materials use continuous fibers, such as carbon fibers, in a matrix. These fibers are much larger than carbon nanotubes. Adding f-s-SWNTs to the matrix of a continuous fiber reinforced nanocomposite results in a complex nanocomposite material having improved properties such as improved impact resistance, reduced thermal stress, reduced microcracking, reduced coefficient of thermal expansion, or increased transverse or through-thickness thermal conductivity. Resulting advantages in complex nanocomposite structures include improved durability, improved dimensional stability, elimination of leakage in cryogenic fuel tanks or pressure vessels, improved through-thickness or inplane thermal conductivity, increased grounding or electromagnetic interference (EMI) shielding, increased flywheel energy storage, or tailored radio frequency signature (Stealth), for example. Improved thermal conductivity also could reduce infrared (IR) signature. Further existing materials that demonstrate improved properties by adding f-s-SWNTs include metal particle nanocomposites for electrical or thermal conductivity, nano-clay nanocomposites, or diamond particle nanocomposites, for example.

[0054] *Method of fabricating nanocomposites:* Methods to incorporate nanomaterial into the host matrix include, but are not limited to: (i) in-situ polymerization of monomer(s) of the host polymer in a solvent system in the presence of functionalized solubilized nanomaterial; (ii) mixing both functionalized solubilized nanomaterial and host matrix in a solvent system; or (iii) mixing functionalized solubilized nanomaterial with a host polymer melt.

[0055] A method of forming nanocomposites in accordance with certain embodiments of the present invention includes the use of solvents for dissolving functionalized solubilized nanomaterial and host matrix. A solvent may be organic or aqueous such as, for example, CHCl_3 , chlorobenzene, water, acetic acid, acetone, acetonitrile, aniline, benzene, benzonitrile, benzyl alcohol, bromobenzene, bromoform, 1-butanol, 2-butanol, carbon disulfide, carbon tetrachloride, chlorobenzene, chloroform, cyclohexane, cyclohexanol, decalin, dibromomethane, diethylene glycol, diethylene glycol ethers, diethyl ether, diglyme, dimethoxymethane, N,N-dimethylformamide, ethanol, ethylamine, ethylbenzene, ethylene glycol ethers, ethylene glycol, ethylene oxide, formaldehyde, formic acid, glycerol, heptane, hexane, iodobenzene, mesitylene, methanol, methoxybenzene, methylamine, methylene bromide, methylene chloride, methylpyridine, morpholine, naphthalene, nitrobenzene, nitromethane, octane, pentane, pentyl alcohol, phenol, 1-propanol, 2-propanol, pyridine, pyrrole, pyrrolidine, quinoline, 1,1,2,2-tetrachloroethane, tetrachloroethylene, tetrahydrofuran, tetrahydropyran, tetralin, tetramethylethylenediamine, thiophene, toluene, 1,2,4-trichlorobenzene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, trichloroethylene, triethylamine, triethylene glycol dimethyl ether, 1,3,5-trimethylbenzene, m-xylene, o-xylene, p-xylene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, or N-methyl-2-pyrrolidone.

[0056] Further examples of solvents include ionic liquids or supercritical solvents. Examples of ionic liquids include, for example, tetra-n-butylphosphonium bromide, tetra-n-butylammonium bromide, 1-ethyl-3-methyl-imidazolium chloride, 1-butyl-3-methyl-imidazolium chloride, 1-hexyl-3-methyl-imidazolium chloride, 1-methyl-3-octyl-imidazolium chloride, 1-butyl-4-methyl-pyridinium chloride, 1-ethyl-3-methyl-imidazolium tetrafluoroborate, 1-butyl-3-methyl-imidazolium tetrafluoroborate, 1-hexyl-

3-methyl-imidazolium tetrafluoroborate, 3-methyl-1-octyl-imidazolium tetrafluoroborate, 1-butyl-4-methyl-pyridinium tetrafluoroborate, 1-ethyl-3-methyl-imidazolium hexafluorophosphate, 1-butyl-3-methyl-imidazolium hexafluorophosphate, 1-hexyl-3-methyl-imidazolium hexafluorophosphate, 1-butyl-4-methyl-pyridinium hexafluorophosphate, 1,3-dimethylimidazolium methylsulfate, 1-butyl-3-methyl-imidazolium methylsulfate, dimethylimidazolium triflate, 1-ethyl-3-methylimidazolium triflate, 1-butyl-3-methylimidazolium triflate, 1-butyl-3-ethylimidazolium triflate, or trihexyltetradecylphosphonium chloride. Examples of supercritical solvents include, for example, supercritical carbon dioxide, supercritical water, supercritical ammonia, or supercritical ethylene.

[0057] The functionalized solubilized nanomaterial may comprise an amount by weight or volume of the nanocomposite greater than zero and less than 100%; an amount equal to or within a range of any of the following percentages: 0.01%, 0.02%, 0.04%, 0.05%, 0.075%, 0.1%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0%, 5.5%, 6.0%, 7.0%, 8.0%, 9.0%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, and 75%; an amount by weight or volume of the nanocomposite equal to or greater than 0.1% and less than or equal to 50%; or an amount by weight or volume of the nanocomposite equal to or greater than 1% to 10%.

[0058] The f-s-SWNT mass-fraction loading values for f-s-SWNTs/host matrix nanocomposites are based on pristine SWNT material only and exclude the additive material (the “f-s” material).

[0059] *Percolation threshold:* Nanocomposites of the present invention provide superior electrical or thermal conductivity, or superior mechanical properties as compared with nanocomposites that lack functionalized solubilized nanomaterial. One measure of such nanocomposite properties is the percolation threshold of the nanocomposite. The percolation threshold is the minimum amount by weight or volume of functionalized solubilized nanomaterial present within the host matrix that provides an interconnectivity within the matrix. A low percolation threshold indicates good dispersion of nanomaterial within the host matrix. The percolation threshold is unique to the type of host matrix, type of nanomaterial, type of functionalization/solubilization, and conditions of fabricating the nanocomposites. *The percolation threshold is also unique to a particular property, i.e., a percolation threshold for an electrical property may be different from a percolation threshold for a thermal property for a particular nanocomposite since an electrical property enhancement mechanism is different from a thermal property enhancement mechanism.

[0060] Composites of the present invention demonstrate a percolation threshold for electrical conductivity, or a percolation threshold for thermal conductivity within a range of any of the following percentages: 0.01%, 0.02%, 0.04%, 0.05%, 0.075%, 0.1%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0%, 6%, 7%, 8%, 9%, 10%, 15%, 20%, 25%, 30% and 33% by weight or volume. In other embodiments, a percolation threshold for electrical conductivity or a percolation threshold for thermal conductivity is equal to or greater than 0.01%, 0.02%, 0.04%, 0.05%, 0.1%, 0.5%, 1.0%, 1.5%, 2.0%, 3.0%, 4.0%, 5.0%, 10% and less than or equal to 20.0% by weight or volume. In further embodiments, a percolation threshold for electrical conductivity or a percolation threshold for thermal conductivity is

equal to or greater than 0.01%, 0.02%, 0.04%, 0.05%, 0.1%, 0.5%, 1.0%, 1.5%, 2.0%, 3.0%, 4.0%, and less than or equal to 5.0% by weight or volume.

[0061] Percolation threshold is determined by measuring the property of interest of a nanocomposite versus the mass fraction of loading of functionalized, solubilized nanomaterial into a matrix such as provided in the examples *infra*. For example, the nanocomposite PPE-SWNTs/polystyrene has a percolation threshold for electrical conductivity of 0.045 wt% of SWNT loading, while the nanocomposite PPE-SWNTs/polycarbonate has a percolation threshold for electrical conductivity of 0.11 wt% of SWNT loading.

[0062] *Nanocomposites for electrical applications:* Nanocomposite embodiments of the present invention have an electrical conductivity percolation threshold that is lower than that of the nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial. By providing electrical conductivity at acceptable loadings, embodiments of the present invention make possible applications such as electrostatic dissipation, electrostatic painting, electromagnetic interference (EMI) shielding, printable circuit wiring, transparent conductive coatings.

[0063] Articles of manufacture comprising a nanocomposite of the present invention include wire, printable circuit wire, coatings, transparent coatings, coatings for resist materials, resist materials, films, fibers, powders, inks, ink jettable nanocomposite solutions, paints, electrosprayed paints, EMI shields, conductive sealants, conductive caulks, conductive adhesives, opto-electronic devices, for example, and other articles for electrically conductive applications such as electrostatic dissipation, electrostatic painting, or electromagnetic interference (EMI) shielding, for example.

[0064] *Nanocomposites for thermal applications:* Nanocomposite embodiments of the present invention have a thermal conductivity percolation threshold that is lower than that of the nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial. Enhanced thermal conductivity provides many applications. Nanocomposite materials can be engineered to be more compliant and conforming, thus providing much better heat transfer to take advantage of the high thermal conductivity in the material. Therefore, nanocomposites herein are useful for heat transfer, either heating or cooling, or packaging, for example.

[0065] Articles of manufacture comprising a nanocomposite of the present invention include electronics, photonics, microelectromechanical (MEMS) packaging, heat spreaders, heat sinks, packages, modules, heat pipes, housings, enclosures, heat exchangers, radiant heaters, thermal interface materials, heat spreaders, films, fibers, powders, coatings, automotive applications including, for example, under-hood components, radiators, sensor housings, electronic modules, or fuel cells, industrial applications, including, for example, electrical coil components, pump parts, electric motor parts, transformers, piping, tubing, or heating, ventilation or air conditioning (HVAC) equipment.

[0066] For example, a heat transfer application using nanocomposites of the present invention as a thermal interface between an integrated circuit ("IC") (or IC package) and an accompanying heat sink is shown in FIG. 5A and FIG. 5B and includes heatsink 10, TIM2 20 (thermal-interface material over the integrated heat spreader), integrated heat spreader 30 (HIS), TIM1 40 (thermal-interface material over the

die), die 50, underfill 60, and substrate 70. FIG. 5A shows an example thermal-solution architecture that is typically used in laptop applications. The example architecture of FIG. 5A comprises heatsink 10, TIM1 (thermal-interface material over the die) 40, die 50, underfill 60, and substrate 70. FIG. 5B shows another example thermal-solution architecture that is typically used in desktop and server applications. The example architecture of FIG. 5B comprises heatsink 10, TIM2 (thermal-interface material over the integrated heat spreader) 20, integrated heat spreader (HIS) 30, TIM1 (thermal-interface material over the die) 40, die 50, underfill 60, and substrate 70. For example, nanocomposites of the present invention may be used in TIM1 40 or TIM2 20 in the architectures of FIG. 5A and FIG. 5B.

[0067] The thermal conductivity properties provided by nanocomposites of the present invention make the nanocomposites suitable for cooling electrical components, such as in the example architectures of FIG. 5A and FIG. 5B, by effectively conducting heat away from the component (e.g., to a heat sink 10). In certain embodiments, the nanocomposite interface (e.g., TIM1 40 and/or TIM2 20) may be implemented as a solid material (e.g., a solid sheet) that is formed to fit in the architecture in a desired manner. In other embodiments, the nanocomposite interface may be implemented as a viscous (e.g., “gooey”) substance.

[0068] *Nanocomposites for mechanical applications:* Nanocomposite embodiments of the present invention have an improved mechanical property, such as any one of tensile stress, tensile strain, stiffness, strength, fracture toughness, creep resistance, creep rupture resistance, and fatigue resistance, as compared to that of the nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial. By providing an improved mechanical property at acceptable loadings, embodiments of the present invention make various mechanical applications possible.

[0069] Articles of manufacture comprising a nanocomposite of the present invention include adhesives, reinforced continuous fiber materials, aircraft structures, aircraft gas turbine engine components, spacecraft structures, instrument structures, missiles, launch vehicle structures, reusable launch vehicle cryogenic fuel tanks fitting attachment, compressed natural gas and hydrogen fuel tanks, ship and boat structures, pressure vessel fitting attachment, sporting goods, industrial equipment, automotive and mass transit vehicles, offshore oil exploration and production equipment, wind turbine blades, medical equipment (e.g. x-ray tables), orthotics, prosthetics, films, fibers, powders, or furnitures.

[0070] *Nanocomposites having low percolation thresholds for more than one property or more than one improved property:* While a nanocomposite of the present invention may have different percolation thresholds for different properties, a nanocomposite may have low percolation thresholds for more than one property and therefore provide multiple advantageous properties. For example, a nanocomposite may have an increased electrical conductivity at a low f-s-SWNT loading and, in addition, an enhanced mechanical or thermal property at that loading. Due to the multifunctional nature of f-s-SWNTs, nanocomposites herein may be useful for one or more than one of electrical, mechanical, thermal, chemical, sensing and actuating applications, for example.

[0071] Adhesives are widely used to assemble electronics. In many applications, they must be electrical insulators. However, there many applications for which electrical conductivity is desirable or at least

acceptable. There are also strong drivers for adhesives with improved thermal conductivity. For example, diamond particle-reinforced adhesives are now used in production applications. Based on the advantageous thermal conductivity of nanocomposites herein, this could be an important application. In instances where high thermal conductivity is desirable, but electrical insulation is required, very thin electrically insulating interfaces can be used in conjunction with nanocomposites so that the multi-layered structure would provide both electrical insulation and high thermal conductivity.

[0072] Further articles of manufacture comprising nanocomposites of the present invention include aircraft structures, aircraft gas turbine engine components, spacecraft structures, instrument structures, missiles, launch vehicle structures, reusable launch vehicle cryogenic fuel tanks, ship or boat structures, sporting goods, industrial equipment, automotive or mass transit vehicles, offshore oil exploration or production equipment, wind turbine blades, medical equipment (e.g. x-ray tables), orthotics, or prosthetics, for example.

[0073] The process of noncovalent functionalization of carbon nanotubes used in the present examples for making nanocomposite materials is described by Chen, J. *et al.* (*J. Am. Chem. Soc.*, 124, 9034 (2002)) which process results in excellent nanotube dispersion. SWNTs produced by high pressure carbon monoxide process (HiPco) were purchased from Carbon Nanotechnologies, Inc. (Houston, TX), and were solubilized in chloroform with poly(phenyleneethynylene)s (PPE) along with vigorous shaking and/or short bath-sonication as described by Chen *et al.* (*ibid*) and in U.S. patent application US 2004/0034177 published February 19, 2004, having USSN 10/255,122, filed September 24, 2002, and U.S. patent application USSN 10/318,730 filed December 13, 2002. For the present examples, the PPE was provided by Haiying Liu (Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931).

[0074] The following examples are presented to further illustrate various aspects of the present invention, and are not intended to limit the scope of the invention.

Example 1

Electrical Conductivity of Nanocomposites of Polymer and Functionalized, Solubilized Nanomaterial

[0075] Noncovalently functionalized, soluble SWNTs/polymer nanocomposites of the present example show improvements in electrical conductivity over the polymer itself, with very low percolation thresholds (0.05-0.1 wt% of SWNT loading).

[0076] PPE-functionalized SWNT solutions were mixed with a host polymer (polycarbonate or polystyrene) solution in chloroform to give a homogeneous nanotube/polymer nanocomposite solution. A uniform nanocomposite film was prepared from this solution on a silicon wafer with a 100 nm thick thermal oxide layer either by drop casting or by slow-speed spin coating. The samples were then heated to 80 °C to 90 °C to remove residual solvent.

[0077] Nanotube polymer nanocomposite films with various amounts of solubilized and functionalized SWNT loadings from 0.01 wt% to 10 wt% in polystyrene as well as in polycarbonate were prepared.

Thicknesses of the films were measured using a LEO 1530 Scanning Electron Microscope or a profilometer. A typical thickness of a nanocomposite film was in the range of 2-10 μm . The SWNT mass-fraction loading values for f-s-SWNTs/host polymer nanocomposites are based on pristine SWNT material only and exclude the additive material. **FIG. 1A** and **FIG. 1B** show scanning electron microscope (SEM) images of the surface (**1A**) and the cross section (**1B**) of PPE-SWNTs/polystyrene nanocomposite film (5 wt% SWNTs) prepared by solution casting. The images show excellent dispersion of PPE-functionalized SWNTs in host polymer matrix. f-s-SWNTs are randomly distributed not only along the surface (**FIG. 1A**), but also through the cross section (**FIG. 1B**), indicating the formation of an isotropic, three dimensional nanotube network in host polymer matrix, thereby allowing for the possibility that the nanocomposites demonstrate isotropic electrical conductivity. The films show individual and bundles of f-s-SWNTs uniformly mixed in the polymer matrix.

[0078] Electrical conductivity measurements were performed using a standard four point probe method to reduce the effects of contact resistance. A Phillips DM 2812 power supply and a Keithly 2002 digital multimeter were used to measure the current-voltage characteristics of the samples.

[0079] Composites prepared using PPE functionalized nanotubes exhibit very low percolation thresholds and many orders of increase in electrical conductivity. **FIG. 2A** shows the measured volume conductivity of PPE-SWNTs/polystyrene nanocomposites as a function of the SWNT loading and formed in accordance with an embodiment of the present invention. The conductivity of the composite increases sharply between 0.02 wt% to 0.05 wt% SWNT loading, indicating the formation of a percolating network. At the onset of percolating network, the electrical conductivity obeys the power law relation

$$\sigma_c \propto (v - v_c)^\beta \quad (1)$$

where σ_c is the composite conductivity, v is the SWNT volume fraction, v_c is the percolation threshold and β is the critical exponent. The densities of the polymer and the SWNT are similar, therefore, the mass fraction m and volume fraction v of the SWNT in the polymer are assumed to be the same. As shown in **FIG. 2B**, the PPE-SWNTs/polystyrene conductivity agrees very well with the percolation behavior of equation (1) above. The straight line with $m_c=0.045\%$ and $\beta = 1.54$ gives an excellent fit to the data with a correlation factor of 0.994, indicating an extremely low percolation threshold at 0.045 wt% of SWNT loading. The very low percolation threshold is a signature of excellent dispersion of high aspect ratio soluble f-s-SWNTs. For comparison, the conductivity of pure polystyrene is about 10^{-14} S/m (C. A. Harper, *Handbook of Plastics, Elastomers, and Composites*, 4th ed. (McGraw-Hill, 2002)), and the conductivity of pristine (unfunctionalized) HiPco-SWNT buckypaper is about 5.1×10^4 S/m. Buckypaper is not a nanocomposite as used herein since there is no host polymer present.

[0080] In addition to the very low percolation threshold, the conductivity of the nanocomposite reached 6.89 S/m at 7 wt% of SWNT loading, which is 14 orders of magnitude higher than that (10^{-14} S/m) of pure polystyrene. The conductivity of 6.89 S/m at 7 wt% of SWNT loading is 5 orders of magnitude higher than that of a nonfunctionalized SWNTs(8.5 wt%)/polystyrene nanocomposite (1.34×10^{-5} S/m) that was prepared by in situ polymerization (H. J. Barraza, *et al.*, *Nano Lett.* 2, 797 (2002)). In contrast to the *in*

situ polymerization technique, this method of using functionalized carbon nanotube to obtain highly dispersed nanocomposite is applicable to various host matrices and does not require lengthy sonication procedures.

[0081] FIG. 3A and FIG. 3B show the electrical conductivity (measured volume conductivity) of PPE-SWNTs/polycarbonate nanocomposites as a function of the SWNT loading for nanocomposites prepared by the same procedure as that of FIG. 2A and FIG. 2B. The conductivity of PPE-SWNTs/polycarbonate is generally higher than that of PPE-SWNTs/polystyrene at the same SWNT loading. For example, the conductivity reached 4.81×10^2 S/m at 7 wt% of SWNT loading, which is 15 orders of magnitude higher than that of pure polycarbonate (about 10^{-13} S/m, C. A. Harper, *ibid.*). For polycarbonate nanocomposites, as shown in FIG. 3B, a very low percolation threshold of 0.11 wt% of SWNT loading was observed ($m_c=0.11\%$; $\beta=2.79$).

[0082] FIG. 2A and FIG. 3A also show conductivity levels for electrical applications such as electrostatic dissipation, electrostatic painting and EMI shielding (Miller, *Plastics World*, 54, September, 73 (1996)). As shown in FIG. 3A, 0.3 wt% of SWNT loading in polycarbonate is sufficient for applications such as electrostatic dissipation and electrostatic painting, and 3 wt% of SWNT loading is adequate for EMI shielding applications. Since only a very low f-s-SWNT loading is required to achieve the cited conductivity levels, the host polymer's other preferred physical properties and processability would be minimally compromised within the nanocomposite.

[0083] In contrast to previous techniques (M. J. Biercuk, et al., *Appl. Phys. Lett.* 80, 2767 (2002)); Park, C. et al., *Chem. Phys. Lett.*, 364, 303 (2002); Barraza, H.J. et al., *Nano Letters*, 2, 797 (2002)) the present process is applicable to assembly of various different polymer matrices and the dispersion of nanotubes is very uniform. The high conductivity levels indicate that the electrical properties of the carbon nanotubes are not affected by the nanocomposite. Further, the lengths of carbon nanotubes are preserved due to the absence of lengthy sonication procedures.

Example 2

Thermal Conductivity of Nanocomposites of Polymer and Functionalized, Solubilized Nanomaterial

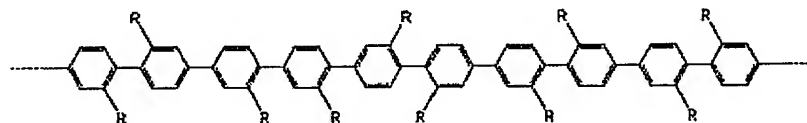
[0084] Noncovalently functionalized, soluble SWNTs/polymer nanocomposites of the present example show improvements in thermal conductivity as compared to that of the polymer itself.

[0085] Thermal conductivity was measured on nanocomposites with various amounts of SWNT loadings from 0.5 wt% to 10 wt%. Films of the nanocomposites were prepared by solution casting on a PTFE substrate and the free standing films were peeled off from the substrate. A typical film thickness was about 50-100 microns. Out-of-plane thermal conductivity was measured using a commercial Hitachi Thermal Conductivity Measurement System (Hitachi, Ltd., 6, Kanda-Surugadai 4-chome, Chiyoda-ku, Tokyo 101-8010, Japan). At room temperature, f-s-SWNTs/polycarbonate nanocomposite film at 10 wt% of SWNTs loading results in ~ 35% increase in out-of-plane thermal conductivity as compared to that of pure polycarbonate film.

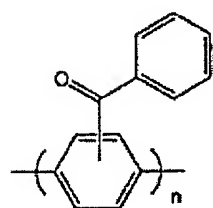
Example 3
Mechanical Properties of Nanocomposites of Polymer and
Functionalized, Solubilized Nanomaterial

[0086] The present example provides improved mechanical properties of nanocomposites of f-s-SWNTs and polymer as compared with that of the polymer itself.

[0087] The term, PARMAX® (Mississippi Polymer Technologies, Inc., Bay Saint Louis, MS), refers to a class of thermoplastic rigid-rod polymers that are soluble in organic solvents and melt processable. PARMAX® is based on a substituted poly(1,4-phenylene) in which each phenylene ring has a substituted organic group R. The general structure of PARMAX® is shown at I.

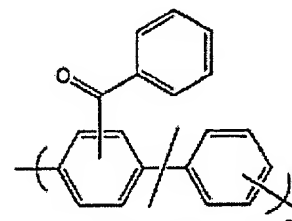


I.



Parmax® -1000

II.



Parmax® -1200

III.

[0088] The monomer of PARMAX®-1000 is shown at II. and the monomer of PARMAX®-1200 is shown at III.

[0089] A PARMAX®-1200 solution in chloroform was mixed with a PPE-SWNT solution in chloroform. The solution was cast on a substrate, for example, glass, and let dry to form a film. The film was further dried under vacuum and at a temperature appropriate for the solvent; for chloroform, ambient temperature is appropriate.

[0090] The mechanical properties of the nanocomposite were measured using an Instron Mechanical Testing System (Model 5567, Instron Corporation Headquarters, 100 Royall Street, Canton, MA, 02021, USA). The results showed that 2 wt% of SWNTs reinforcement in the nanocomposite results in ~ 29% increase in tensile strength (from 154 to 199 MPa), and ~ 51% increase in Young's modulus (from 3.9 to 5.9 GPa) compared to the PARMAX® material itself.

[0091] Further, pure polycarbonate film and f-s-SWNTs (2 wt% of SWNTs)/polycarbonate film were prepared by the solution casting on PTFE substrate. Mechanical measurements were done as cited *supra*.

FIG. 6A shows the mechanical property of tensile stress vs. tensile strain for pure polycarbonate film, and FIG. 6B shows the mechanical property of tensile stress vs. tensile strain for f-s-SWNTs (2 wt% of SWNTs)/polycarbonate film. For example, the 2 wt% of SWNTs filling results in 79% increase in tensile strength of polycarbonate, and the break strain (tensile strain) is increased by approximately a factor of 10.

[0092] In addition to the film-casting method, the PPE-SWNT/ PARMAX® nanocomposite can also be manufactured by other methods, such as compression molding, extrusion, or fiber spinning, for example. In one method, a PARMAX®-1200 solution in chloroform was mixed with a PPE-SWNT solution in chloroform to form a uniform solution of PPE-SWNTs/ PARMAX® nanocomposite. Ethanol was added to the PPE-SWNTs/ PARMAX® nanocomposite solution with vigorous stirring to precipitate the nanocomposite. After filtration and drying, a uniform powder of PPE-SWNTs/ PARMAX® nanocomposite was obtained. The resulting nanocomposite powder is fabricated into a variety of shaped-solids by compression molding at 200–400 °C (preferably 315 °C) for ~ 30 min.

[0093] FIG. 4 shows a fracture surface in an f-s-SWNTs/polycarbonate nanocomposite. The nanotubes remain in the matrix even after the fracture, indicating strong interaction with the host polymer. Raw nanotubes often interact poorly with a matrix, that is, a fracture expels them and leaves behind voids in the material.

Example 4 Improved Properties of Nanocomposites of Two Host Polymers and Functionalized, Solubilized Nanomaterial

[0094] The present example provides improved mechanical and electrical properties of nanocomposites of f-s-SWNTs and two host polymers as compared with that of one host polymer.

[0095] A comparison was made between nanocomposites comprising f-s-SWNTs/epoxy and f-s-SWNTs/epoxy plus polycarbonate as host polymer(s) regarding electrical and mechanical properties. The nanocomposites were assembled from epoxy resin, epoxy hardener, PPE-SWNTs, and with or without polycarbonate. The processing steps are dispersing PPE-SWNTs and epoxy resin, hardener, and 5% by weight of the final composition of polycarbonate (in those compositions that contain polycarbonate) and stirring or shaking until the mixture is well dispersed to form a nanocomposite. For films, the mixture was either solution-cast or spin-coated and the solvent was removed by evaporation to produce a nanocomposite film with excellent nanotube dispersion.

[0096] Resulting mechanical and electrical properties are shown in Table 1 for solvent cast films of approximately 50 micrometers thickness.

Table 1. Mechanical and Electrical Properties of Nanocomposite Films Having Two Host Polymers and Functionalized, Solubilized Nanomaterial

Film	SWNT loading	Young's Modulus	Tensile Strength at	Electrical Conductivity
------	-----------------	--------------------	------------------------	----------------------------

	(wt%)	(GPa)	Break (MPa)	(S/m)
Epoxy SC-15	0	0.42	16.0	10^{-14}
f-s-SWNTs/epoxy (no polycarbonate)	5	0.75	22.2	0.053
f-s-SWNTs/epoxy + 5 wt% polycarbonate	5	1.23	46.3	1.17

[0097] The effectiveness of adding f-s-SWNTs to epoxy is apparent from the data of Table 1 that show the electrical conductivity of epoxy film alone to be 10^{-14} S/m and that of epoxy with functionalized solubilized nanotubes to be 5.3×10^{-2} S/m, an increase of about 12 orders of magnitude. Film having epoxy and f-s-SWNTs provides a modest improvement in mechanical properties over that of epoxy alone (Young's modulus is 0.75 GPa for the nanocomposite and 0.42 GPa for the epoxy film, and tensile strength is 22.2 MPa for the nanocomposite and 16.0 MPa for the epoxy film), possibly because of voids in the film.

[0098] The effectiveness of adding polycarbonate to the f-s-SWNTs and epoxy is apparent from the data of Table 1 that show the mechanical properties improved about two-fold (Young's modulus is 1.23 GPa for the two-polymer-composite and 0.75 GPa for the one-polymer-composite, and tensile strength is 46.3 MPa for the two-polymer-composite and 22.2 MPa for the one-polymer-composite). Film having the two-polymer nanocomposite provides about a 20-fold improvement in electrical conductivity over that of the one-polymer-composite (1.17 S/m for the two-polymer nanocomposite as compared to 0.053 for the one-polymer-composite).

[0099] Other embodiments of the present invention will be apparent to those skilled in the art from a consideration of this specification or practice of the embodiments disclosed herein. However, the foregoing specification is considered merely exemplary of the present invention with the true scope and spirit of the invention being indicated by the following claims.

[0100] As used herein and unless otherwise indicated, the terms "a" and "an" are taken to mean "one", "at least one" or "one or more".

WHAT IS CLAIMED IS:

1. A nanocomposite, comprising:
a host matrix comprising polymer matrix or nonpolymer matrix, and
functionalized, solubilized nanomaterial dispersed within the host matrix,
wherein the nanocomposite has an electrical conductivity percolation threshold or a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.
2. The nanocomposite of Claim 1 wherein the nanocomposite has an electrical conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.
3. The nanocomposite of Claim 1 wherein the nanocomposite has a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.
4. The nanocomposite of Claim 1 wherein the host matrix is a polymer matrix and the polymer matrix comprises a thermoplastic polymer, a thermoset polymer, or a combination thereof.
5. The nanocomposite of Claim 1 wherein the host matrix is a polymer matrix and the polymer matrix comprises an inorganic polymer matrix.
6. The nanocomposite of Claim 5 wherein the inorganic polymer matrix comprises silicone, polysilane, polycarbosilane, polygermane, polystannane, polyphosphazene, or a combination thereof.
7. The nanocomposite of Claim 1 wherein the host matrix is a polymer matrix and the polymer matrix comprises a nylon, polyethylene, polyisoprene, sbs rubber, polydicyclopentadiene, polytetrafluoroethylene, poly(phenylene sulfide), silicone, aramid, cellulose, rayon, poly(methyl methacrylate), poly(vinylidene chloride), poly(vinylidene fluoride), carbon fiber, polyisobutylene, polychloroprene, polybutadiene, polypropylene, poly(vinyl chloride), poly(vinyl acetate), polystyrene, polyvinylpyrrolidone, polycyanoacrylate, polyacrylonitrile, poly(aryleneethynylene), poly(phenyleneethynylene), polythiophene, polyaniline, polypyrrole, polyphenylene, ethylene vinyl alcohol, fluoroplastic, ionomer, polyacrylate, polybutadiene, polybutylene, polyethylene, polyethylenechlorinate, polymethylpentene, polypropylene, polystyrene, polyvinylchloride, polyvinylidene chloride, polyamide, polyamide-imide, polyaryletherketone, polycarbonate, polyketone, polyester, polyetheretherketone, polyetherimide, polyethersulfone, polyimide, polyphenylene oxide,

polyphenylene sulfide, polyphthalamide, polysulfone, polyethylene terephthalate, epoxy resin, polyurethane, or a combination thereof.

8. The nanocomposite of Claim 7 wherein the polymer matrix comprises a polystyrene.
9. The nanocomposite of Claim 7 wherein the polymer matrix comprises a polyphenylene.
10. The nanocomposite of Claim 7 wherein the polymer matrix comprises a polycarbonate.
11. The nanocomposite of Claim 7 wherein the polymer matrix comprises a fluoroplastic and the fluoroplastic comprises polytetrafluoroethylene, fluoroethylene propylene, perfluoroalkoxyalkane, chlorotrifluoroethylene, ethylene chlorotrifluoroethylene, ethylene tetrafluoroethylene, or a combination thereof.
12. The nanocomposite of Claim 1 wherein the functionalized, solubilized nanomaterial comprises a functionalized and solubilized single-walled carbon nanotube, multi-walled carbon nanotube, carbon nanoparticle, carbon nanosheet, carbon nanofiber, carbon nanorope, carbon nanoribbon, carbon nanofibril, carbon nanoneedle, carbon nanohorn, carbon nanocone, carbon nanoscroll, carbon nanodot, or a combination thereof.
13. The nanocomposite of Claim 1 wherein the functionalized, solubilized nanomaterial comprises a functionalized and solubilized single-walled boron nitride nanotube, multi-walled boron nitride nanotube, boron nitride nanoparticle, boron nitride nanosheet, boron nitride nanofiber, boron nitride nanorope, boron nitride nanoribbon, boron nitride nanofibril, boron nitride nanoneedle, boron nitride nanohorn, boron nitride nanocone, boron nitride nanoscroll, a boron nitride nanodot, or a combination thereof.
14. The nanocomposite of Claim 1 wherein the functionalized, solubilized nanomaterial comprises a functionalized and solubilized graphite nanoplatelet, a functionalized and solubilized fullerene material, or a combination thereof.
15. The nanocomposite of Claim 1 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.01% and less than or equal to 75.0% by weight or volume of the nanocomposite.
16. The nanocomposite of Claim 1 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.04% and less than or equal to 50.0% by weight or volume of the nanocomposite.

17. The nanocomposite of Claim 1 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.1% and less than or equal to 10.0% by weight or volume of the nanocomposite.
18. The nanocomposite of Claim 1 wherein the functionalized, solubilized nanomaterial of the nanocomposite is a first filler and the nanocomposite further comprises a second filler to form a complex nanocomposite,
wherein the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and
the second filler is other than a functionalized, solubilized nanomaterial.
19. The nanocomposite of Claim 1 wherein the host matrix is a first host polymer matrix and the nanocomposite further comprises a second host polymer matrix,
wherein the functionalized, solubilized nanomaterial is dispersed within the first and second host polymer matrices, and
wherein the nanocomposite has an electrical conductivity percolation threshold or a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the first and second host polymer matrices and nanomaterial other than the functionalized, solubilized nanomaterial.
20. The nanocomposite of Claim 19 wherein the first host polymer matrix is an epoxy and the second host polymer matrix is a polycarbonate.
21. An article of manufacture comprising the nanocomposite of Claim 1.
22. An article of manufacture comprising the nanocomposite of Claim 2.
23. An article of manufacture comprising the nanocomposite of Claim 3.
24. An article of manufacture comprising the nanocomposite of Claim 12.
25. An article of manufacture comprising the nanocomposite of Claim 18.
26. An article of manufacture comprising the nanocomposite of Claim 19.
27. The article of manufacture of Claim 21 wherein the article of manufacture comprises a fiber.
28. The article of manufacture of Claim 21 wherein the article of manufacture comprises a film.

29. The article of manufacture of Claim 21 wherein the article of manufacture comprises a powder.
30. The article of manufacture of Claim 24 wherein the article of manufacture comprises a fiber.
31. A method of increasing electrical or thermal conductivity of a host matrix comprising a polymer matrix or nonpolymer matrix, the method comprising:
dispersing functionalized, solubilized nanomaterial within host matrix material to form a nanocomposite
wherein the nanocomposite has an electrical conductivity percolation threshold or a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.
32. The method of Claim 31 wherein the host matrix material is the host matrix.
33. The method of Claim 31 wherein the host matrix material comprises a monomer of a host polymer matrix and the method further comprises the step of polymerizing the host polymer matrix material in the presence of the functionalized, solubilized nanomaterial.
34. The method of Claim 31 wherein the host matrix is a first host polymer matrix and the method further comprises:
dispersing a second host polymer matrix material with functionalized, solubilized nanomaterial and with first host polymer matrix material to form a nanocomposite comprising a first host polymer matrix and a second host polymer matrix,
wherein the nanocomposite has an electrical conductivity percolation threshold or a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the first and second host polymer matrices and nanomaterial other than the functionalized, solubilized nanomaterial.
35. The method of Claim 34 wherein the first host polymer matrix material is the first host polymer matrix and the second host polymer matrix material is the second host polymer matrix.
36. The method of Claim 34 wherein the first host polymer matrix material comprises a monomer of the first host polymer matrix material, the second host polymer matrix material comprises a monomer of the second host polymer matrix material, and the method further comprises the step of polymerizing the host polymer matrix material in the presence of the functionalized, solubilized nanomaterial.
37. The method of Claim 31 wherein the nanocomposite has an electrical conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.

38. The method of Claim 31 wherein the nanocomposite has a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.

39. The method of Claim 31 wherein the host matrix material comprises a thermoplastic polymer or monomer thereof, or a thermoset polymer, or monomer thereof, or a combination thereof.

40. The method of Claim 31 wherein the host matrix is a polymer matrix and the polymer matrix comprises an inorganic polymer matrix.

41. The method of Claim 40 wherein the inorganic polymer matrix comprises silicone, polysilane, polycarbosilane, polygermane, polystannane, a polyphosphazene, or a combination thereof.

42. The method of Claim 31 wherein the host matrix comprises a host polymer matrix material comprising a nylon, polyethylene, polyisoprene, sbs rubber, polydicyclopentadiene, polytetrafluoroethylene, poly(phenylene sulfide), silicone, aramid, cellulose, rayon, poly(methyl methacrylate), poly(vinylidene chloride), poly(vinylidene fluoride), carbon fiber, polyisobutylene, polychloroprene, polybutadiene, polypropylene, poly(vinyl chloride), poly(vinyl acetate), polystyrene, polyvinylpyrrolidone, polycyanoacrylate, polyacrylonitrile, poly(aryleneethynylene), poly(phenyleneethynylene), polythiophene, polyaniline, polypyrrole, polyphenylene, ethylene vinyl alcohol, fluoroplastic, ionomer, polyacrylate, polybutadiene, polybutylene, polyethylene, polyethylenedichloride, polymethylpentene, polypropylene, polystyrene, polyvinylchloride, polyvinylidene chloride, polyamide, polyamide-imide, polyaryletherketone, polycarbonate, polyketone, polyester, polyetheretherketone, polyetherimide, polyethersulfone, polyimide, polyphenylene oxide, polyphenylene sulfide, polyphthalamide, polysulfone, polyethylene terephthalate, epoxy resin, or a polyurethane, or monomer thereof, or a combination thereof.

43. The method of Claim 42 wherein the host polymer matrix material comprises a polystyrene, or monomer thereof.

44. The method of Claim 42 wherein the host polymer matrix material comprises a polyphenylene, or monomer thereof.

45. The method of Claim 42 wherein the host polymer matrix material comprises a polycarbonate, or monomer thereof.

46. The method of Claim 42 wherein the host polymer matrix material comprises a fluoroplastic and the fluoroplastic comprises polytetrafluoroethylene, fluoroethylene propylene, perfluoroalkoxyalkane, chlorotrifluoroethylene, ethylene chlorotrifluoroethylene, or ethylene tetrafluoroethylene, or monomer thereof, or combination thereof.

47. The method of Claim 31 wherein the functionalized, solubilized nanomaterial comprises a functionalized, solubilized single-walled carbon nanotube, multi-walled carbon nanotube, carbon nanoparticle, carbon nanosheet, carbon nanofiber, carbon nanorope, carbon nanoribbon, carbon nanofibril, carbon nanoneedle, carbon nanohorn, carbon nanocone, carbon nanoscroll, carbon nanodot, or a combination thereof.

48. The method of Claim 31 wherein the functionalized, solubilized nanomaterial comprises a functionalized, solubilized single-walled boron nitride nanotube, multi-walled boron nitride nanotube, boron nitride nanoparticle, boron nitride nanosheet, boron nitride nanofiber, boron nitride nanorope, boron nitride nanoribbon, boron nitride nanofibril, boron nitride nanoneedle, boron nitride nanohorn, boron nitride nanocone, boron nitride nanoscroll, a boron nitride nanodot, or a combination thereof.

49. The method of Claim 31 wherein the functionalized, solubilized nanomaterial comprises a functionalized, solubilized graphite nanoplatelet, a functionalized, solubilized fullerene material, or a combination thereof.

50. The method of Claim 31 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.01% and less than or equal to 75.0% by weight or volume of the nanocomposite.

51. The method of Claim 31 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.04% and less than or equal to 50.0% by weight or volume of the nanocomposite.

52. The method of Claim 31 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.1% and less than or equal to 10.0% by weight or volume of the nanocomposite.

53. The method of Claim 31 wherein the functionalized, solubilized nanomaterial is a first filler, and the dispersing further comprises

dispersing a second filler within host matrix material to form a complex nanocomposite, wherein the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and

wherein the second filler is other than a functionalized, solubilized nanomaterial.

54. The method of Claim 34 wherein the first host polymer matrix is an epoxy polymer and the second host polymer matrix is a polycarbonate polymer.

55. A product produced by a method of Claim 31.

56. A product produced by a method of Claim 34.

57. A product produced by a method of Claim 53.

58. A nanocomposite, comprising:
a host matrix of polymer matrix or nonpolymer matrix, wherein the polymer matrix is other than polystyrene and polycarbonate, and
functionalized, solubilized nanomaterial dispersed within the host matrix,
wherein the nanocomposite has a mechanical property that is enhanced as compared to that of a nanocomposite comprising the host matrix and the nanomaterial other than the functionalized, solubilized nanomaterial.

59. The nanocomposite of Claim 58 wherein the host matrix is a polymer matrix and the polymer matrix comprises a thermoplastic polymer, a thermoset polymer, or a combination thereof.

60. The nanocomposite of Claim 58 wherein the host matrix is a polymer matrix and the polymer matrix comprises an inorganic polymer matrix.

61. The nanocomposite of Claim 58 wherein the host matrix is a polymer matrix and the host polymer matrix comprises a nylon, polyethylene, polyisoprene, sbs rubber, polydicyclopentadiene, polytetrafluoroethylene, poly(phenylene sulfide), silicone, aramid, cellulose, rayon, poly(methyl methacrylate), poly(vinylidene chloride), poly(vinylidene fluoride), carbon fiber, polyisobutylene, polychloroprene, polybutadiene, polypropylene, poly(vinyl chloride), poly(vinyl acetate), polystyrene, polyvinylpyrrolidone, polycyanoacrylate, polyacrylonitrile, poly(aryleneethynylene), poly(phenyleneethynylene), polythiophene, polyaniline, polypyrrole, polyphenylene, ethylene vinyl alcohol, fluoroplastic, ionomer, polyacrylate, polybutadiene, polybutylene, polyethylene, polyethylenechlorinate, polymethylpentene, polypropylene, polyvinylchloride, polyvinylidene chloride, polyamide, polyamide-imide, polyaryletherketone, polyketone, polyester, polyetheretherketone, polyetherimide, polyethersulfone, polyimide, polyphenylene oxide, polyphenylene sulfide, polyphthalamide, polysulfone, polyethylene terephthalate, epoxy resin, a polyurethane, or a combination thereof.

62. The nanocomposite of Claim 58 wherein the host polymer matrix comprises a polyphenylene.
63. The nanocomposite of Claim 58 wherein the host polymer matrix comprises a fluoroplastic and the fluoroplastic comprises polytetrafluoroethylene, fluoroethylene propylene, perfluoroalkoxyalkane, chlorotrifluoroethylene, ethylene chlorotrifluoroethylene, ethylene tetrafluoroethylene, or a combination thereof.
64. The nanocomposite of Claim 58 wherein the host matrix is a first host polymer matrix and the nanocomposite further comprises a second host polymer matrix, wherein the functionalized, solubilized nanomaterial is dispersed within the first and second host polymer matrices, and wherein the nanocomposite has a mechanical property that is enhanced as compared to that of a nanocomposite comprising the first and second host polymer matrices and nanomaterial other than the functionalized, solubilized nanomaterial.
65. The nanocomposite of Claim 58 wherein the functionalized, solubilized nanomaterial comprises a functionalized and solubilized single-walled carbon nanotube, multi-walled carbon nanotube, carbon nanoparticle, carbon nanosheet, carbon nanofiber, carbon nanorope, carbon nanoribbon, carbon nanofibril, carbon nanoneedle, carbon nanohorn, carbon nanocone, carbon nanoscroll, carbon nanodot, or a combination thereof.
66. The nanocomposite of Claim 58 wherein the functionalized, solubilized nanomaterial comprises a functionalized and solubilized single-walled boron nitride nanotube, multi-walled boron nitride nanotube, boron nitride nanoparticle, boron nitride nanosheet, boron nitride nanofiber, boron nitride nanorope, boron nitride nanoribbon, boron nitride nanofibril, boron nitride nanoneedle, boron nitride nanohorn, boron nitride nanocone, boron nitride nanoscroll, a boron nitride nanodot, or a combination thereof.
67. The nanocomposite of Claim 58 wherein the functionalized, solubilized nanomaterial comprises a functionalized, solubilized graphite nanoplatelet, a functionalized, solubilized fullerene material, or a combination thereof.
68. The nanocomposite of Claim 58 wherein the functionalized, solubilized nanomaterial comprises an amount of equal to or greater than 0.01% and less than or equal to 75.0% by weight or volume of the nanocomposite.

69. The nanocomposite of Claim 58 wherein the functionalized, solubilized nanomaterial comprises an amount of equal to or greater than 0.04% and less than or equal to 50.0% by weight or volume of the nanocomposite.

70. The nanocomposite of Claim 58 wherein the functionalized, solubilized nanomaterial of the nanocomposite is a first filler and the nanocomposite further comprises a second filler to form a complex nanocomposite,
wherein the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and
the second filler is other than a functionalized, solubilized nanomaterial.

71. A nanocomposite, comprising:
a polystyrene, and
functionalized, solubilized nanomaterial dispersed within the polystyrene,
wherein the nanocomposite has a mechanical property that is enhanced as compared to that of a nanocomposite comprising the host matrix and the nanomaterial other than the functionalized, solubilized nanomaterial.

72. The nanocomposite of Claim 71 wherein the polystyrene is a first host polymer matrix and the nanocomposite further comprises a second host polymer matrix,
wherein the functionalized, solubilized nanomaterial is dispersed within the first and second host polymer matrices, and
wherein the nanocomposite has a mechanical property that is enhanced as compared to that of a nanocomposite comprising the first and second host polymer matrices and nanomaterial other than the functionalized, solubilized nanomaterial.

73. The nanocomposite of Claim 71 wherein the functionalized, solubilized nanomaterial comprises a functionalized, solubilized single-walled carbon nanotube, multi-walled carbon nanotube, carbon nanoparticle, carbon nanosheet, carbon nanofiber, carbon nanorope, carbon nanoribbon, carbon nanofibril, carbon nanoneedle, carbon nanohorn, carbon nanocone, carbon nanoscroll, carbon nanodot, or a combination thereof.

74. The nanocomposite of Claim 71 wherein the functionalized, solubilized nanomaterial comprises an amount of equal to or greater than 0.01% and less than or equal to 75.0% by weight or volume of the nanocomposite.

75. The nanocomposite of Claim 71 wherein the functionalized, solubilized nanomaterial comprises an amount of equal to or greater than 0.04% and less than or equal to 50.0% by weight or volume of the nanocomposite.

76. A nanocomposite, comprising:

a host matrix comprising a first polymer matrix and a second polymer matrix wherein the first polymer matrix is polycarbonate, and

functionalized, solubilized nanomaterial dispersed within the host matrix,

wherein the nanocomposite has a mechanical property that is enhanced as compared to that of a nanocomposite comprising the host matrix and the nanomaterial other than the functionalized, solubilized nanomaterial.

77. The nanocomposite of Claim 76 wherein the functionalized, solubilized nanomaterial comprises a functionalized and solubilized single-walled carbon nanotube, multi-walled carbon nanotube, carbon nanoparticle, carbon nanosheet, carbon nanofiber, carbon nanorope, carbon nanoribbon, carbon nanofibril, carbon nanoneedle, carbon nanohorn, carbon nanocone, carbon nanoscroll, carbon nanodot, or a combination thereof.

78. The nanocomposite of Claim 76 wherein the functionalized, solubilized nanomaterial comprises an amount of equal to or greater than 0.01% and less than or equal to 75.0% by weight or volume of the nanocomposite.

79. The nanocomposite of Claim 76 wherein the functionalized, solubilized nanomaterial comprises an amount of equal to or greater than 0.04% and less than or equal to 50.0% by weight or volume of the nanocomposite.

80. The nanocomposite of Claim 76 wherein the functionalized, solubilized nanomaterial of the nanocomposite is a first filler and the nanocomposite further comprises a second filler to form a complex nanocomposite

wherein the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and

the second filler is other than a functionalized, solubilized nanomaterial.

81. An article of manufacture comprising the nanocomposite of claim 58.

82. An article of manufacture comprising the nanocomposite of claim 60.

83. An article of manufacture comprising the nanocomposite of claim 61.

84. A method of improving a mechanical property of a host matrix comprising polymer matrix or nonpolymer matrix, wherein the host matrix is other than polystyrene or polycarbonate, the method comprising:

dispersing functionalized, solubilized nanomaterial within host matrix material to form a nanocomposite

wherein the nanocomposite has an improved mechanical property compared to that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.

85. The method of Claim 84 wherein the host matrix material is the host matrix.

86. The method of Claim 84 wherein the host matrix material comprises a monomer of the host matrix and the method further comprises the step of polymerizing the host matrix material in the presence of the functionalized, solubilized nanomaterial.

87. The method of Claim 84 wherein the host matrix is a first host polymer matrix and the method further comprises:

dispersing a second host polymer matrix material with functionalized, solubilized nanomaterial and with first host polymer matrix material to form a nanocomposite comprising a first host polymer matrix and a second host polymer matrix,

wherein the nanocomposite has an improved mechanical property compared to that of a nanocomposite comprising the first and second host polymer matrices and nanomaterial other than the functionalized, solubilized nanomaterial.

88. The method of Claim 87 wherein the first host polymer matrix material is the first host polymer matrix.

89. The method of Claim 87 wherein the first host polymer matrix material comprises a monomer of the first host polymer matrix material and the method further comprises the step of polymerizing the host polymer matrix material in the presence of the functionalized, solubilized nanomaterial.

90. The method of Claim 84 wherein the host polymer matrix material comprises a thermoplastic polymer or monomer thereof, a thermoset polymer resin, or monomer thereof, or a combination thereof.

91. The method of Claim 84 wherein the host matrix is a polymer matrix and the polymer matrix comprises an inorganic polymer matrix.

92. The method of Claim 91 wherein the inorganic polymer matrix comprises silicone, polysilane, polycarbosilane, polygermane, polystannane, a polyphosphazene, or a combination thereof.
93. The method of Claim 84 wherein the host matrix comprises a host polymer matrix material comprising a nylon, polyethylene, polyisoprene, sbs rubber, polydicyclopentadiene, polytetrafluoroethylene, poly(phenylene sulfide), silicone, aramid, cellulose, rayon, poly(methyl methacrylate), poly(vinylidene chloride), poly(vinylidene fluoride), carbon fiber, polyisobutylene, polychloroprene, polybutadiene, polypropylene, poly(vinyl chloride), poly(vinyl acetate), polystyrene, polyvinylpyrrolidone, polycyanoacrylate, polyacrylonitrile, poly(aryleneethynylene), poly(phenyleneethynylene), polythiophene, polyaniline, polypyrrole, polyphenylene, ethylene vinyl alcohol, fluoroplastic, ionomer, polyacrylate, polybutadiene, polybutylene, polyethylene, polyethylenechlorinate, polymethylpentene, polypropylene, polyvinylchloride, polyvinylidene chloride, polyamide, polyamide-imide, polyaryletherketone, polyketone, polyester, polyetheretherketone, polyetherimide, polyethersulfone, polyimide, polyphenylene oxide, polyphenylene sulfide, polyphthalamide, polysulfone, polyethylene terephthalate, epoxy resin, or a polyurethane, or monomer thereof, or a combination thereof.
94. The method of Claim 93 wherein the host polymer matrix material comprises a polyphenylene, or monomer thereof.
95. The method of Claim 93 wherein the host polymer matrix material comprises a fluoroplastic and the fluoroplastic comprises polytetrafluoroethylene, fluoroethylene propylene, perfluoroalkoxyalkane, chlorotrifluoroethylene, ethylene chlorotrifluoroethylene, or ethylene tetrafluoroethylene, or monomer thereof, or combination thereof.
96. The method of Claim 84 wherein the functionalized, solubilized nanomaterial comprises a functionalized, solubilized single-walled carbon nanotube, multi-walled carbon nanotube, carbon nanoparticle, carbon nanosheet, carbon nanofiber, carbon nanorope, carbon nanoribbon, carbon nanofibril, carbon nanoneedle, carbon nanohorn, carbon nanocone, carbon nanoscroll, carbon nanodot, or a combination thereof.
97. The method of Claim 84 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.01% and less than or equal to 75.0% by weight or volume of the nanocomposite.
98. The method of Claim 84 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.04% and less than or equal to 50.0% by weight or volume of the nanocomposite.

99. The method of Claim 84 wherein the functionalized, solubilized nanomaterial is a first filler, and the dispersing further comprises

dispersing a second filler within host matrix material to form a complex nanocomposite, wherein the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and wherein the second filler is other than a functionalized, solubilized nanomaterial.

100. A product produced by the method of Claim 84.

101. A product produced by the method of Claim 87.

102. A product produced by the method of Claim 99.

103. A method of improving a mechanical property of a polystyrene, the method comprising:
dispersing functionalized, solubilized nanomaterial within styrene polymeric material to form a nanocomposite

wherein the nanocomposite has an improved mechanical property compared to that of a nanocomposite comprising the polystyrene and nanomaterial other than the functionalized, solubilized nanomaterial.

104. The method of Claim 103 wherein the styrene polymeric material is the polystyrene.

105. The method of Claim 103 wherein the styrene polymeric material comprises a monomer of the polystyrene and the method further comprises the step of polymerizing the material in the presence of the functionalized, solubilized nanomaterial.

106. The method of Claim 103 wherein the polystyrene is a first host polymer matrix and the method further comprises

dispersing a second host polymer matrix material with functionalized, solubilized nanomaterial and with first host polymer matrix material to form a nanocomposite comprising a first host polymer matrix and a second host polymer matrix,

wherein the nanocomposite has an improved mechanical property compared to that of a nanocomposite comprising the first and second host polymer matrices and nanomaterial other than the functionalized, solubilized nanomaterial.

107. The method of Claim 103 wherein the functionalized, solubilized nanomaterial comprises a functionalized, solubilized single-walled carbon nanotube, multi-walled carbon nanotube, carbon nanoparticle, carbon nanosheet, carbon nanofiber, carbon nanorope, carbon nanoribbon, carbon

nanofibril, carbon nanoneedle, carbon nanohorn, carbon nanocone, carbon nanoscroll, carbon nanorod, or a combination thereof.

108. The method of Claim 103 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.01% and less than or equal to 75.0% by weight or volume of the nanocomposite.

109. The method of Claim 103 wherein the functionalized, solubilized nanomaterial comprises an amount equal to or greater than 0.04% and less than or equal to 50.0% by weight or volume of the nanocomposite.

110. The method of Claim 103 wherein the functionalized, solubilized nanomaterial is a first filler, and the dispersing further comprises

dispersing a second filler within host matrix material to form a complex nanocomposite, wherein the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and wherein the second filler is other than a functionalized, solubilized nanomaterial.

111. A product produced by the method of Claim 103.

112. A product produced by the method of Claim 110.

113. A method of improving a mechanical property of a host matrix comprising a first polymer matrix and a second polymer matrix wherein the first polymer matrix is polycarbonate, the method comprising:

dispersing functionalized, solubilized nanomaterial within host polymeric material to form a nanocomposite

wherein the nanocomposite has an improved mechanical property compared to that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.

114. The method of Claim 113 wherein the functionalized, solubilized nanomaterial is a first filler, and the dispersing further comprises

dispersing a second filler within host matrix material to form a complex nanocomposite, wherein the second filler comprises a continuous fiber, a discontinuous fiber, a nanoparticle, a microparticle, a macroparticle, or a combination thereof, and wherein the second filler is other than a functionalized, solubilized nanomaterial.

115. A product produced by a method of Claim 113.

116. A product produced by a method of Claim 114.
117. An article of manufacture comprising the nanocomposite of Claim 64.
118. An article of manufacture comprising the nanocomposite of Claim 65.
119. An article of manufacture comprising the nanocomposite of Claim 70.
120. An article of manufacture comprising the nanocomposite of Claim 71.
121. An article of manufacture comprising the nanocomposite of Claim 76.
122. A nanocomposite, comprising:
a host matrix comprising nonpolymer matrix, and
functionalized, solubilized nanomaterial dispersed within the host matrix,
wherein the nanocomposite has an electrical conductivity percolation threshold or a thermal conductivity percolation threshold that is lower than that of a nanocomposite comprising the host matrix and nanomaterial other than the functionalized, solubilized nanomaterial.
123. The nanocomposite of Claim 122 wherein the nonpolymer matrix comprises a ceramic matrix.
124. The nanocomposite of Claim 122 wherein the nonpolymer matrix comprises a metal matrix.
125. A nanocomposite, comprising:
a host matrix comprising nonpolymer matrix, and
functionalized, solubilized nanomaterial dispersed within the host matrix,
wherein the nanocomposite has a mechanical property that is enhanced as compared to that of a nanocomposite comprising the host matrix and the nanomaterial other than the functionalized, solubilized nanomaterial.
126. The nanocomposite of Claim 125 wherein the nonpolymer matrix comprises a ceramic matrix.
127. The nanocomposite of Claim 125 wherein the nonpolymer matrix comprises a metal matrix.
128. An article of manufacture comprising the nanocomposite of Claim 122.
129. An article of manufacture comprising the nanocomposite of Claim 125.

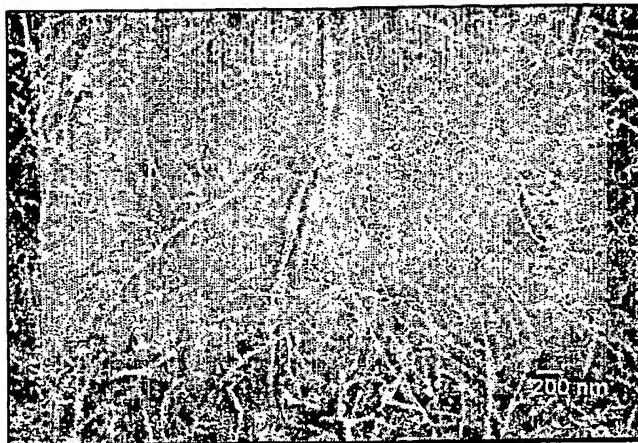


FIG. 1A

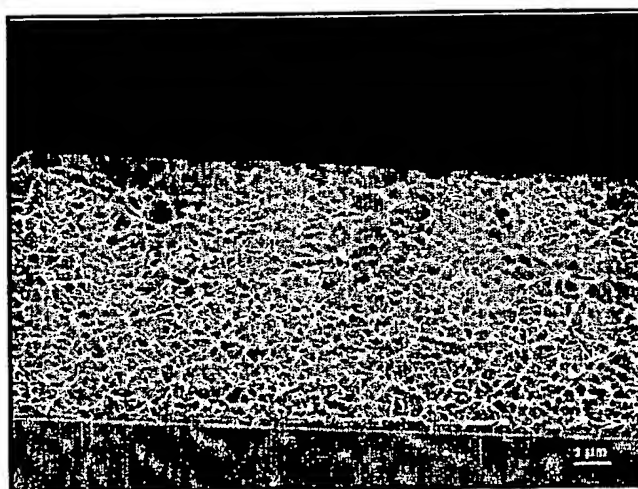


FIG. 1B

2/6

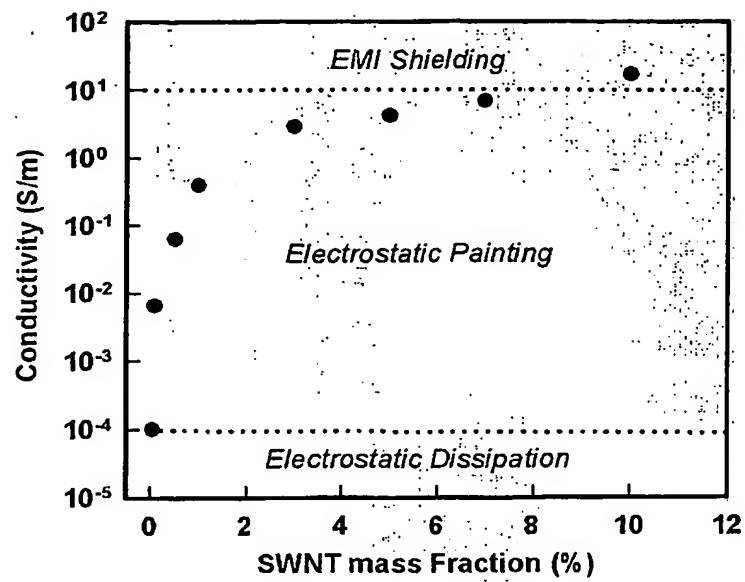


FIG. 2A

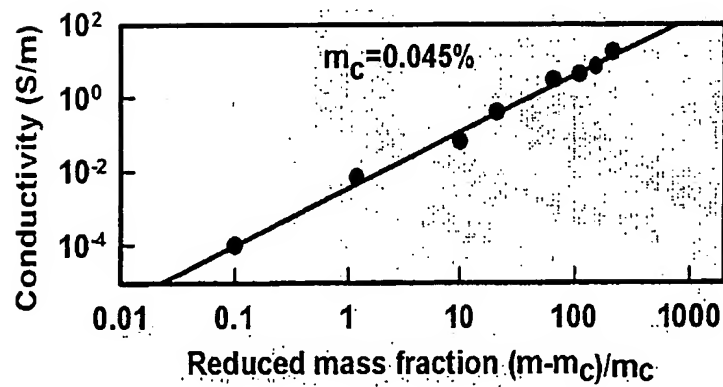


FIG. 2B

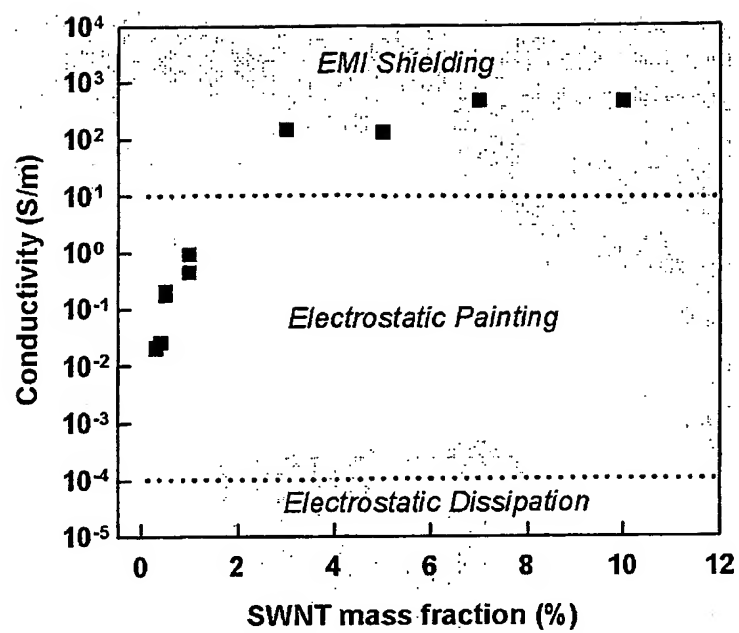


FIG. 3A

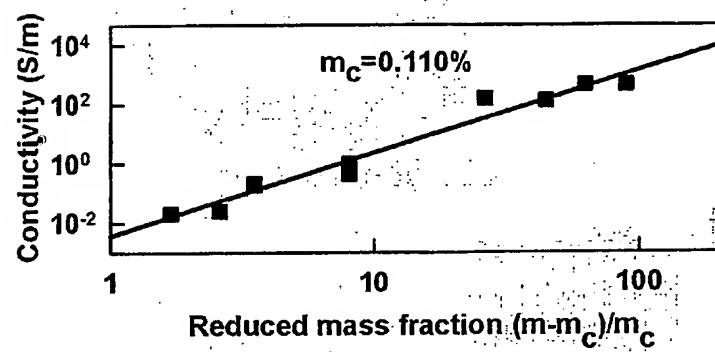


FIG. 3B

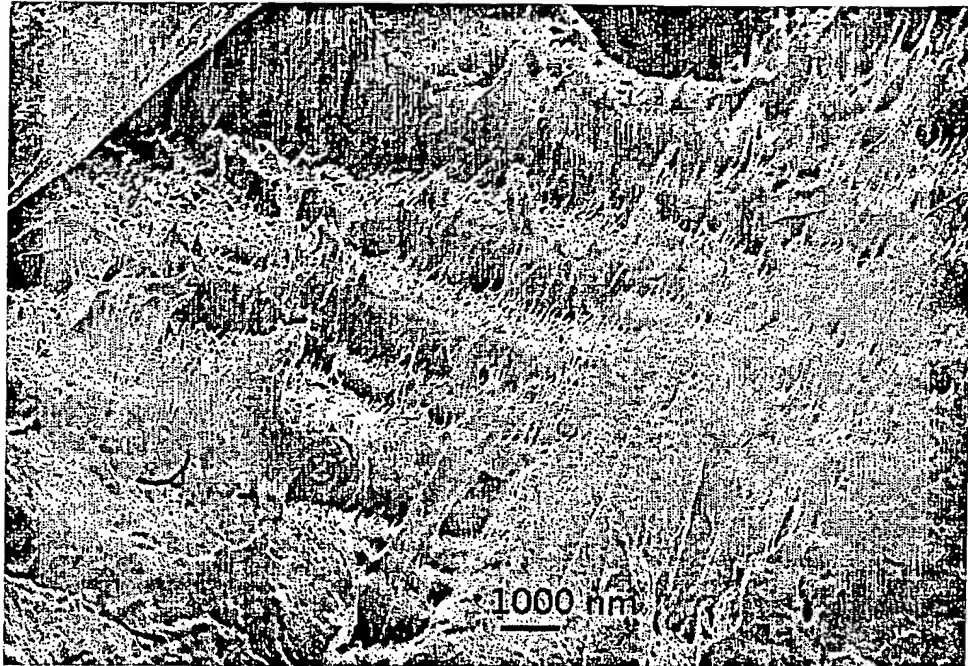


FIG. 4

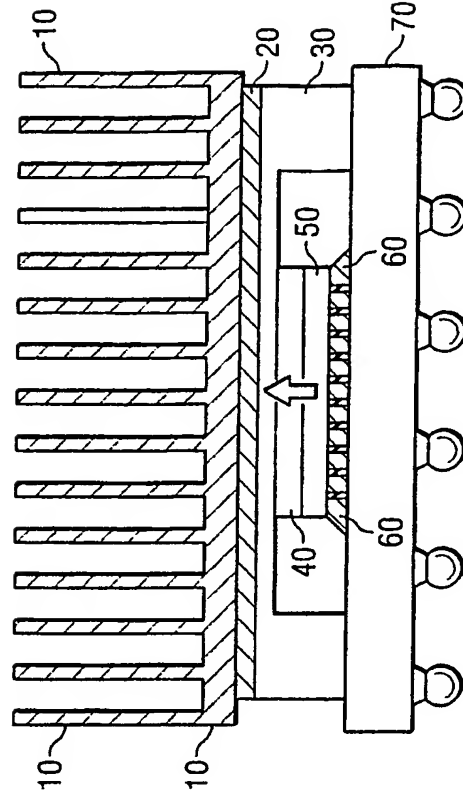


FIG. 5B

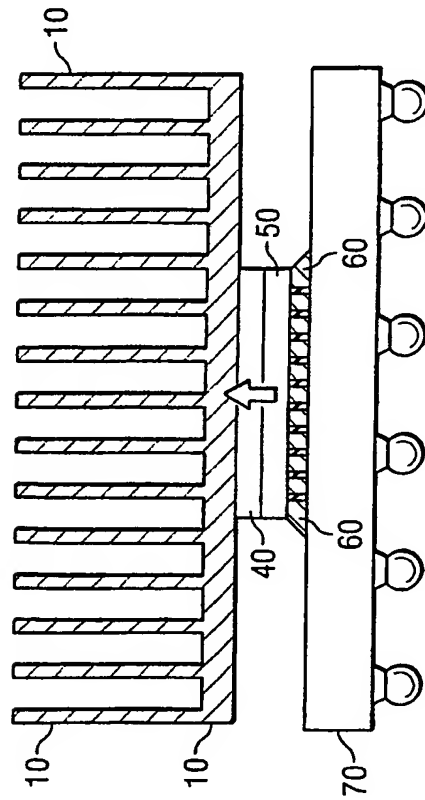


FIG. 5A

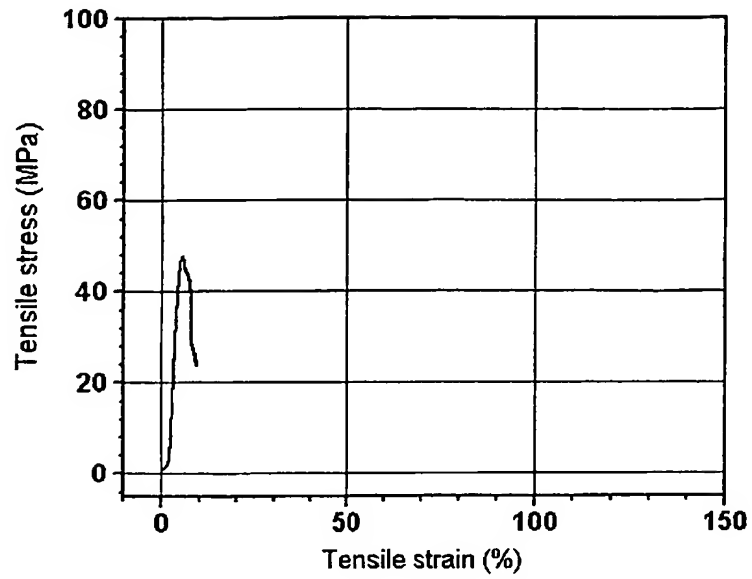


FIG. 6A

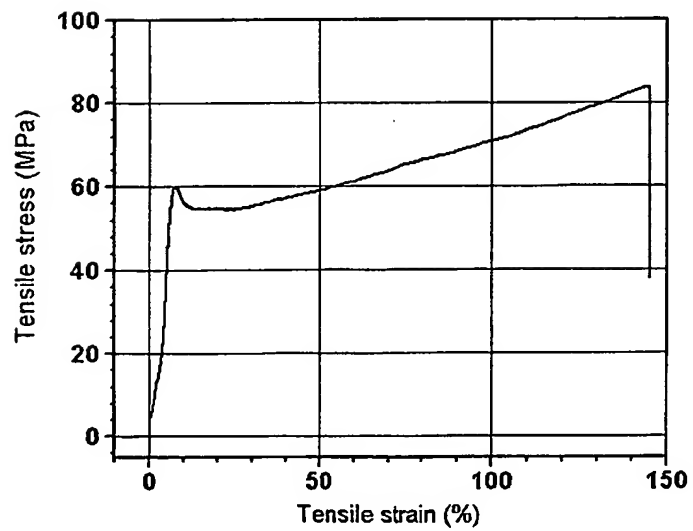


FIG. 6B

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(71) Applicant (for all designated States except US): ZYVEX
CORPORATION [US/US]; 1321 N. Plano Road,
Richardson, TX 75081 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CHEN, Jian
[CN/US]; 411 Buckingham, #434, Richardson, TX 75081
(US). RAJAGOPAL, Ramasubramaniam [IN/US]; 2600
East Renner Road, #163, Richardson, TX 75082 (US).

(74) Agents: MCCOMBS, David L. et al.; Haynes and Boone,
LLP, Suite 3100, 901 Main Street, Dallas, TX 75202 (US).

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kind of national protection available): AE, AG, AL, AM,
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GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii)) for the following designations AE,
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ,
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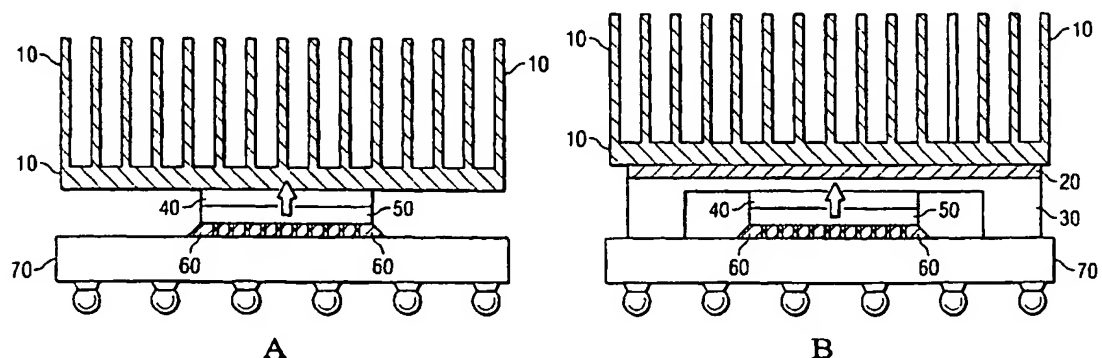
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For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
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(54) Title: NANOCOMPOSITES AND METHOD FOR PRODUCTION



(57) Abstract: Electrical, thermal and mechanical applications are provided for nanocomposite materials having low percolation thresholds for electrical conductivity, low percolation thresholds for thermal conductivity, or improved mechanical properties.

WO 2004/106420 A3

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K3/00 C08K3/04 C08K3/38 C08K9/00 C08K7/24
C01B31/02 C01B31/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal; WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/048632 A1 (O'CONNELL MICHAEL ET AL) 25 April 2002 (2002-04-25) paragraphs [0021] - [0024], [0033] - [0035], [0045] - [0057]; claims 1-46; examples 1-13	1-12, 14-47, 49-65, 67-129
X	US 2002/046872 A1 (O'CONNELL MICHAEL ET AL) 25 April 2002 (2002-04-25) paragraphs [0021] - [0024], [0033] - [0035], [0045] - [0057]; claims 1-50; examples 1-13 ----- -/--	1-12, 14-47, 49-65, 67-129

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 October 2004

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European Patent Office, P.B. 5818 Patentlaan 2
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Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2001/010809 A1 (CHEN JIAN ET AL) 2 August 2001 (2001-08-02) paragraphs [0008] - [0013]; claims 1-36 -----	1-12, 14-47, 49-65, 67-129
X	US 6 187 823 B1 (CHEN JIAN ET AL) - 13 February 2001 (2001-02-13) column 1, line 49 - column 2, line 57; claims 1-15 -----	1-12; 14-47, 49-65, 67-129
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X	WO 02/076888 A (YERUSHALMI-ROZEN RACHEL ; REGEV OREN (IL); UNIV BEN GURION (IL)) 3 October 2002 (2002-10-03) page 1, line 25 - page 4, line 4 page 5, line 10 - page 6, line 32 page 8, line 22 - page 9, line 2; claims 1-22; examples 1-7 -----	1-12, 14-47, 49-65, 67-129
X	HIRSCH A: "FUNCTIONALIZATION OF SINGLE-WALLED CARBON NANOTUBES" ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, VERLAG CHEMIE. WEINHEIM, DE, vol. 41, no. 11, 2002, pages 1853-1859, XP001122544 ISSN: 0570-0833 the whole document -----	1-12, 14-47, 49-65, 67-129
X	DE 31 18 503 A (STAEDTLER FA J S) 18 November 1982 (1982-11-18) page 5, line 1 - page 8, line 4; claims 1-19; examples 1,2 -----	1-12, 14-47, 49-65, 67-129
X	US 2002/054995 A1 (MAZURKIEWICZ MARIAN) 9 May 2002 (2002-05-09) paragraphs [0008] - [0011], [0020], [0057], [0108], [0143] - [0148]; claims 24,25; example examples ----- -/--	1-12, 14-47, 49-65, 67-129

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No. , , ,
X	<p>C.J.BRABEC, A.CRAVINO, G.ZERZA, N.C.SARICIFTCI, R.KIEBOOMS, D.VANDERZANDE, J.C.HUMMELEN: "Photoactive blends of poly(para-phenylenevinylene) (PPV) with methanofullerenes from a novel precursor: photophysics and device performance" JOURNAL OF CHEMICAL PHYSICS, vol. 105, 31 January 2001 (2001-01-31), pages 1528-1536, XP002301150 the whole document</p> <p style="text-align: center;">-----</p>	<p>1-12, 14-47, 49-65, 67-129</p>

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-12, 14-47, 49-65, 67-129

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-12,14-47,49-65,67-129

Carbon nanotubes

2. claims: 13,48,66

Boron-nitride nanotubes

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